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DEANSHIP OF GRADUATE STUDIES

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Under the direction of his Thesis Advisor and approved by his Thesis Committee, has been presented to and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of

MASTERS OF SCIENCE IN CHEMICAL ENGINEERING

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DEDICATION

Dedicated To My Parents

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In the name of ALLAH, the Most Beneficent, the Most Merciful.

I would like to acknowledge King Fahd University of Petroleum & Minerals for giving me the opportunity to do my MS and provide support for this research work. I am also grateful to the Chemical Engineering Department for providing the research assistantship.

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THESIS ABSTRACT

Name: MOHAMMAD HASAN IQBAL

Title: Influence of Polymer Type and Structure on Polymer Modification of Saudi Asphalt

Degree: Master of Science

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The influence of polymer type and structure on the properties of polymer modified asphalt (PMA) was studied by rheological techniques. Low density polyethylene (LDPE), ethyl vinyl acetate (EVA), and acrylate polymers were used in this study. The influence of molecular weight (Mw) of LDPE, vinyl acetate (VA) content of EVA, and alkyl acrylate content were investigated. Also, the performance of asphalts modified by LDPE and EVA, similar viscosity, were compared. Polymer modification significantly improved the rheological properties of the base asphalt. Temperature susceptibility of base asphalt was decreased in the case of EVA and acrylate polymer modification. Polymer type did not have strong influence on the ageing of PMA. EVA modified asphalt showed hardening behavior. Acrylate PMA showed more hardening behavior at high temperature than LDPE. All the polymers showed better storage stability when used to modify with asphalt; however, LDPE with high M_w was the best. Performance grading of modified asphalt showed that the service temperature window of the base asphalt increased and exceeded the value required in the Gulf region. Asphalt concrete mix (ACM) tests were performed, and PMA was found to show better rutting resistance in comparison to base asphalt. ACM of LDPE showed poor rutting resistance. On the other hand, ethyl acrylate polymer showed the best rutting resistance. A direct relation between the elasticity of PMA, and the resilient modulus and rutting resistance of ACM was established.

Master of Science Degree

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الملخص

الإســـم: محمد حسن إقبال
عنوان البحث: تأثير نوع وتركيب البولمر على تحسين مواصفات الأسفلت
الدرجـــة: ماجستير في العلوم الهندسية
القســـم: الهندسة الكيميائية
تاريخ الدرجة: مايو 2004م

في هذا البحث تمت دراسة تأثير نوعية التركيب الجزئي للبولمر على تحسين مواصفات الأسفلت بإستخدام الطرق الريولوجيه. استخدمت في هذه الدراسة عدة بولمرات منها البولي إيثلين قليل الكثافة وبأوزان جزيئية مختلفة. كما تم إستخدام متعدد أستات الفنيل وكذلك أستخدمت بولمرات الأكرلات. وتمت دراسة تأثير كمية البولمر في تحسين خواص الأسفلت عند درجة الحرارة العالية وكذلك على خواصه التخزينية. وجد أن كل البولمرات تحسن من خواص الأسفلت بمستويات مختلفة. ولكن وضح أن بولي أستات الفنيل والذي يحتوي على جزء قليل من أستات الفنيل هو الأحسن أداء في تحسين مواصفات الأسفلت في أداء الخلطات الخرسانية، من حيث مقاومة التخدد والمرونة ومقاومة الحرارة العالية. وقد وجد أن خواص الأسفلت والخلطات الأسفلتية الناتجة عن استخدام هذا البولمر تفوق المواصفات المطلوبة لمنطقة الخليج.

Chapter 1

INTRODUCTION

Asphalts are multiphase systems with rheological behavior resembling that of the low-molecular-weight polymers (Rozeveld et. al., 1997). Because of the complexity of this material, the complete internal structure of asphalt is not yet known. There are two types of asphalt, natural and artificial. Artificial asphalts are derived from petroleum and contain many functional groups.

The primitive structure model of asphalt is a combination of maltenic and aspahltenic phases. Maltene is a mixture of different hydrocarbons, ranging from aliphatic to aromatic species. In a broad sense, asphalt consists of three main constituents: oil, resins and asphaltenes. Oils in asphalt have the lowest molecular weight (25-800 g/mol) and have a large number of saturated side chains and few rings. Resins are the intermediate molecular weight compounds (800-2000 g/mol), which contain sulfur and nitrogen. Asphaltenes are the highest molecular weight compounds (1800-8000 g/mol) with aromatic ring structures, few side chains and functional groups, which may react with potential polymer modifiers (Lee et al., 1997). An average asphalt sample has an asphaltene/resin/oil ratio of approximately 23/27/50 and asphaltene content is higher for harder asphalt. From the beginning of the twentieth century, asphalt has been considered

to be a colloid containing micelles-asphaltenes surrounded by a layer of lower molecular weight hydrocarbons dispersed in oils (Stastna et al., 2003). It is considered that a micelle in asphalt consists of a single asphaltene molecule surrounded by resin molecules that are associated with asphaltenes (the interaction being of an electro donor and acceptor type).

The majority part of the world's asphalt production is used by the paving industry. Because of the availability of relatively low coast binders, the roadway networks in the Gulf Countries have developed rapidly than those of many other industrialized countries (Al-Dubabe et al., 1998). Aggregate (94-96 wt%) and asphalt binder (4-6 wt%) are the conventional materials of hot mix asphalt concrete (HMAC). This small amount of asphalt binder influences pavement performance more than the aggregate because of the environmental factors, such as heat and sun radiation (Al-Dubabe et al., 1998). The increase in road traffic during the last two decades in combination with an insufficient degree of maintenance has caused an accelerated deterioration of road structures in many countries (Isacsson et al., 1995). To minimize the deterioration and thereby to increase the long term durability of a flexible pavement, the asphalt layers should be improved with regard to performance-related properties, such as resistance to permanent deformation, low temperature cracking, load-associated fatigue, wear, stripping and ageing. Moreover, for certain applications, such as bridges, runways and surfaces with high traffic loading, special binders are urgently required (Lu and Isacsson, 1997). With the increasing of traffic load various improvements of the engineering properties of asphalt are sought.

Asphalt concrete pavement is widely used through all over the world. But asphalt pavements suffer from different types of stress. The most commonly observed types of

distress in asphalt concrete pavements are rutting, fatigue cracking, low temperature cracking, ageing, raveling and stripping (Ait-kadi et al., 1996; Ali et al., 1999 Lu et al., 1998 & 1999; Yousefi et al., 2000; Carreau et al., 2000). Because of its viscoelastic nature, asphalt binder behavior depends on both temperature and rate of loading. At high temperatures, asphalt shows good viscous flow properties with little or no flow resistance, which causes permanent deformation (rutting). At low temperature, asphalt becomes a brittle, elastic solid with little or no viscous properties, which causes thermal cracking. Within the intermediate temperature zone, asphalt usually fails by fatigue cracking, which is caused by repeated loading. In the Kingdom harsh weather conditions affect the asphalt pavement. In addition to that stress on asphalt pavement has increased due to heavy traffic, which enhanced this deterioration. Local asphalts do not meet the required performance grading (PG) at high temperature (76^{o}C). Also, variations of rheological properties with temperature should be reduced. Hence, polymer modification of asphalt is required.

Several additives are being used to increase the performance of asphalt binders. Polymers are the most widely used additives in asphalt modification and give better performance. But polymer asphalt mixer is not compatible. Moreover, asphalt polymer is a complex mixture and the mechanism of action for most of the polymers is insufficiently understood (Isacsson et al., 1995). Polymer-modified asphalt performance depends on the type and amount of polymer, and the asphalt type. Isacsson and Lu (1999) reported that the rheological properties of bitumen are determined by molecular interactions (molecular forces), which in turn depend on chemical compositions. In principle, desired rheological properties of bitumen may be achieved by changing chemical composition

using an additive or chemical reaction modification. The addition of polymers is a versatile way of modifying the rheology of bitumen. In search of polymers that can impart optimum improvement in rheology of asphalt at minimal loading, the miscibility of asphalt with candidate polymers has been recognized as a critical factor (Adedeji et al., 1996). Understanding of the structure of asphalt and its blends with polymers is still incomplete (Stastna et al., 2003). There are different techniques to evaluate the properties of asphalt and modified asphalt. But these results are not consistent (Knorr et al., 2002).

The general objective of this research was to study the effect of polymer type, structure and content on the modification of asphalt. To study the effect of polymer type on asphalt modification, low-density polyethylene (LDPE) polymer and ethyl vinyl acetate (EVA) copolymer were used. In this case, two different grades of LDPE (LD 654 & LD 655) of similar density and different melt index (MI) were used and two different grades of EVA (UL 15019 and UL 15028) polymers of the same MI but different VA content were blended with asphalt. Asphalt was obtained from Saudi Aramco Riyadh Refinery. By measuring the rheological properties of the modified asphalt, the change in viscoelastic properties was compared to observe the effect. Also, polymer modified asphalt concrete mix tests were performed to observe these effects. The effect of acrylate polymer on the polymer modification was also studied. Two different grades of acrylate polymers (Elvaloy 4170 and Elvaloy 3427 AC from Dupont) were blended with asphalt and the corresponding rheological properties will be measured to observe the performance. These two polymers tend to react with asphalt.

NOTE: This thesis is written in paper format. Hence, the reader can skip the following two chapters and go directly to the results and discussion part given in Chapter 4. The first paper is entitled "Influence of M_w of LDPE and Vinyl acetate Content of EVA on the Rheology of Polymer Modified Asphalt", which was accepted for publication in Rheologica Acta. The second paper is entitled as "Rheological Investigation of the Influence of Acrylate Polymers on the Modification of Asphalt". Rheology was the tool of investigation for the papers.

The third paper carries the title "Influence of Polymer Type and Structure on Polymer Modified Asphalt Concrete Mix". In this paper, different standard tests for asphalt concrete mix were performed. In this paper, experimental procedures are similar to second paper; hence, the reader can skip the experimental details in the third paper to avoid repetition.

Chapter 2

LITERATURE REVIEW

To minimize the deterioration of a flexible pavement due to influence from traffic and climate, the bituminous layer should (Isacsson et al., 1995)

a) be stiff enough at elevated temperatures to avoid permanent deformation (rutting)

b) show good fatigue resistance

c) posses good stripping resistance (low water susceptibility)

d) show time independent properties (good ageing properties)

e) have good flexibility at low temperatures (resistance to low temperature cracking)

f) be good wear resistance.

All the performance related properties of the mix are influenced by the binder properties. Brule (1996) mentioned that an ideal binder should have enhanced cohesion and very low temperature susceptibility throughout the range of temperatures to which it will be subjected in service, but low viscosity at the usual temperatures at which it is placed. It was also mentioned that the susceptibility to loading time should be low, whereas its permanent deformation resistance, breaking strength, and fatigue characteristics should be high. In addition, it should have at least the same adhesion

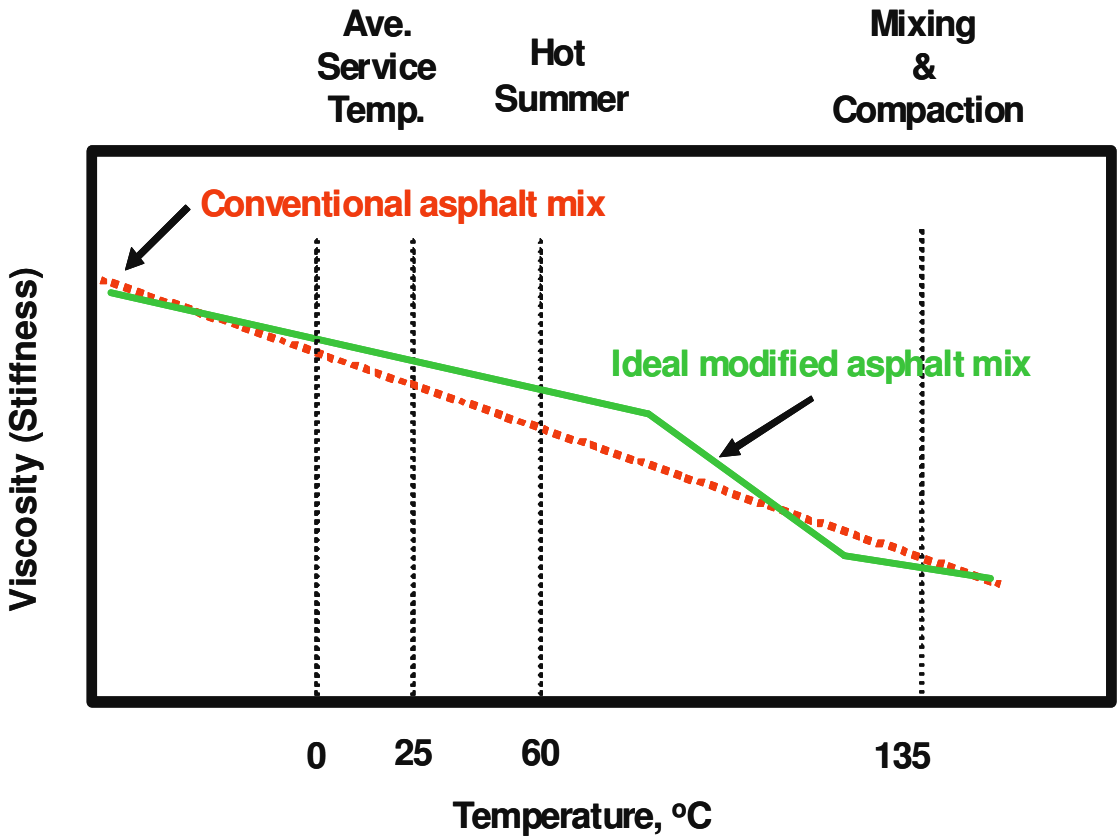


Figure 2.1: Conceptual representations of changes in mixture stiffness can be obtained with an ideal modifier (Terrel and Epps, 1989).

qualities as traditional binders and its ageing characteristics should be good both for laying and in service.

2.1. Needs for Asphalt Modification

The main reason for using these fillers and some other types of modifiers is to improve the performance of paving mixture to meet requirements under prevailing conditions. In the early stage of modification, different grades of asphalts were mixed and delivered better performance. But this mixing was not chemically compatible.

Modifiers have been used in asphalt binders to design against or to repair pavements from the following distresses:

1. Surface defects (Raveling, Stripping).
2. Surface deformation (Rutting, Shoving, Distortion).
3. Cracking (Fatigue cracking, Thermal cracking).

Over the years, many different types of materials have been proposed as additives in bituminous mixes. Table 2.1 shows a compilation of groups of such additives. Different types of chemical reactions can also modify bitumen. The purpose of using a special additive in an asphalt pavement is to achieve better road performance in one or another. Here, only polymer-modified asphalt will be discussed. For most of the groups listed in Table 2.1, a large number of products are commercially available.

2.2. Polymer Modified Asphalt (PMA)

Polymer modification improves the asphalt binder performance. Isacsson (et al., 1998) studied the effect of styrene-butadiene-styrene polymer on low temperature

Table 2.1: Types of asphalt modifications (Isacsson et al., 1995).

	Type		Examples
I.	Additive (excluding polymers) modification	1. Fillers	Lime, carbon black, fly ash
		2. Anti-stripping additives	Organic amines and amides
		3. Extenders	Lignin, sulfur
		5. Anti-oxidants	Zinc anti-oxidants, lead anti-oxidants, phenolics, and amines.
		5. Organo-metal compounds	Organo-mananese compounds, organo-cobalt compounds
		6. Others	Shale oil, Gilsonite, silicone, inorganic fibers
II.	Polymer modification	1. Plastics (a) Thermoplastics.	Polyethylene (PE), Polypropylene (PP), Polyvinyl chloride (PVC), Polystyrene (PS), Ethylene vinyl acetate (EVA).
		(b) Thermosets.	Epoxy resins.
		2.Elastomers (a) Natural rubbers. (b) Synthetic rubbers.	Styrene-butadiene copolymer (SBR), Styrene-butadiene-styrene copolymer (SBS), Ethylene-propylene diene terpolymer (EPDM), Isobutene-isoprene copolymer (IIR).
		3. Reclaimed rubbers	
		4. Fibers	Polyester fibres, Polypropylene fibres
III.	Chemical reaction modification		Addition reaction (bitumen + monomer), Vulcanization (bitumen + sulfur), Nitration reaction (bitumen + nitric acid)

that the importance of polymer modification especially after sufficient period of ageing.

When used as bitumen modifiers, selected polymers alone or blended with bitumen should:

a) be compatible with bitumen

b) resist degradation at asphalt mixing temperatures

c) improve the temperature susceptibility

d) be capable of being processed by conventional mixing and laying equipment

e) give rise to a coating viscosity at normal application temperatures

f) maintain their premium properties during storage, application and in service when blended with bitumen

g) be cost effective

The morphology of asphalt polymer mixture is quite complex. That's why in search of polymers that can impart optimum improvement in rheology of asphalt at minimal loading; the miscibility of asphalt with candidate polymers has been recognized as critical factor. Several investigations have been done regarding miscibility. When asphalt-miscible homopolymers and random copolymers are used, a critical concentration at which polymer entangle is required for asphalt blends to exhibit a network behavior. Triblock or star copolymers (e.g. linear or radial SBS) form a network structure with the minor component polystyrene (PS) end blocks acting as physical cross-links. In asphalt blends with triblock copolymers, such as SBS, have an asphalt compatible poly-butadiene (PB) midblock. Asphalt is anticipated to swell the midblock while maintaining the intrinsic network of the triblock. Such a swollen network is illustrated in Figure 2.2 (a).

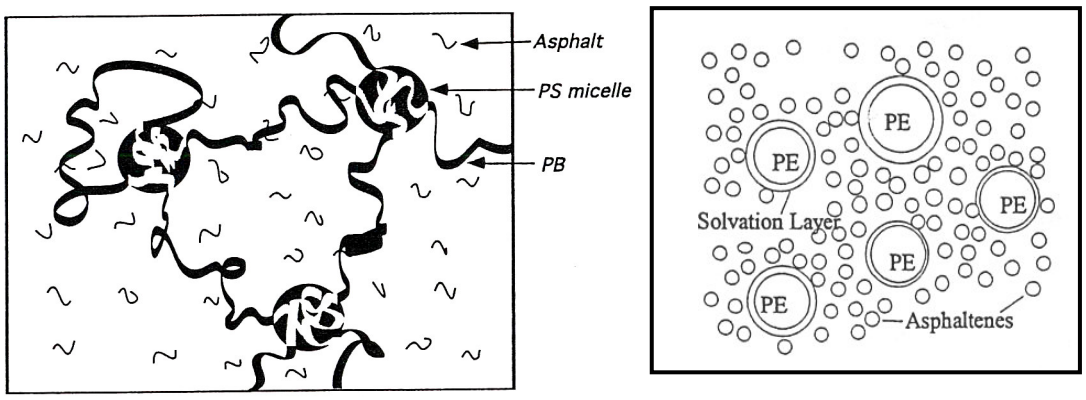


Figure 2.2: Schematic illustration of (a) network in asphalt/SBS blend (Adedeji et. al., 1996) and (b) PE particles in asphalt medium (Yousefi et al., 2000).

In this Figure PS end blocks forming spherical micelles and the PB midblock (connectors of the sphere) are swollen by asphalt oligomer.

A schematic representation of the structure PE-asphalt suspension is illustrated in Figure 2.2 (b). The polymer particles behave as physically active filler that interact with the asphalt medium by absorption and adsorption mechanisms (Yousefi et al., 2000). This results in the penetration of asphalt into the particles, formation of layers, around the particles, and creation of many hollow holes in PE particles after washing out bitumen. It could be concluded that, without network interaction, the improvement of asphalt performance for PE is lesser than that of SBS polymer.

2.3. Background on Rheology

Rheology is the science of deformation and flow of materials. Both viscosity and elasticity can be measured using rheological techniques. Materials can be tested in steady or dynamic shear modes. Dynamic mechanical tests involve the application of a periodically varying (e.g. oscillatory) strain or stress. The general concept of this type of tests is schematically illustrated in Figure 2.3. A sinusoidally varying strain, $\gamma(t)$, usually applied and the output stress, $\tau(t)$, is measured in constant-strain rheometer. The expressions for $\gamma(t)$ and $\tau(t)$ are given below:

$$\gamma(t) = \gamma_o \sin \omega t \qquad (2.3.1)$$

$$\tau(t) = \tau_o \sin(\omega t+\delta) \qquad (2.3.2)$$

Here, γ_o, ω, τ_o, δ and t are strain amplitude, frequency, stress amplitude, phase angle and time respectively. The ratio of the peak stress to the peak strain is defined as the complex modulus, $|G^*|$, or simply denoted G^*, which is the measure of the overall

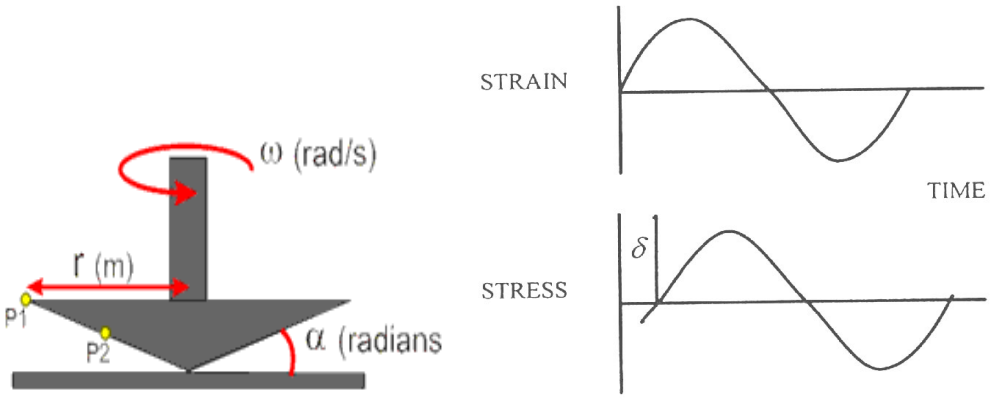


Figure 2.3**:** Cone & plate geometry and sinusoidally varying strain and stress.

resistance to deformation of material. The in-phase component of G* is defined as the storage modulus (G′) and the out-of-phase component as the loss modulus (G″). G′ describes the amount of energy stored released elastically in each oscillation, thus is called the storage modulus, while G″ describes the average energy dissipation-rate, associated with the viscous effects thus is called the loss modulus.

Phase angle (δ) is the phase difference between the stress and strain in an oscillatory deformation and the measure of the viscoelastic character of material. If δ is 90^o, then the binder can be considered purely viscous in nature and, vice versa, δ of 0^o would represent an ideal elastic solid. So, phase angle of viscoelastic materials will be between 0^o and 90^o.

In this situation, a complex viscosity η* can be measured. In general, the complex viscosity contains an elastic component in addition to a term similar to the ordinary steady state viscosity. The complex viscosity is defined by:

$$\eta^* = G^*/i\omega = \eta' - i\eta'' \tag{2.3.3}$$

The dynamic viscosity, η′, is related to steady state viscosity and is the part of the complex viscosity that measures the rate of energy dissipation. Similarly, the imaginary viscosity, η″, measures the elasticity, or stored energy, these two viscosities are computed from the real and imaginary parts of the shear modulus using the following relations,

$$\eta'' = G'/\omega \tag{2.3.4}$$

$$\eta' = G''/\omega \tag{2.3.5}$$

2.4. Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical Analysis is a method that measures the stiffness and mechanical damping (i.e., the internal friction and thermal dissipation) of a cyclically deformed material as a function of temperature, strain and frequency. The combination of stiffness and damping properties is a reflection of the unique viscoelastic nature of polymers. In the DMA test, small cyclic deformations (ω) are applied to the sample in the linear viscoelastic range. The use of dynamic mechanical analysis (DMA), to characterize and evaluate neat and polymer modified asphalt binders, has gained more attention over the last nine years (Al-Dubabe et. al., 1998). This is mainly due to the introduction of the asphalt binder grading system and specifications developed by the Strategic Highway Research Program (SHRP). These new specifications rely heavily on determining the complex shear modulus of fresh and laboratory-aged asphalt samples and the flexural creep stiffness at the highest temperature (rutting) and the lowest temperature (cracking) of the site where the asphalt will be used. Workability and safety of the asphalt binder against flashing is also evaluated.

Isacsson and Ekblad (1999) studied the rheological properties of SEBS, EVA and EBA polymer modified bitumens by dynamic mechanical analysis. They described four different regions of a viscoelastic material by shear modulus. In the glassy region, the binder possesses the highest modulus and is hard and brittle, with little or no intermolecular movement. In the transition region, the binder is resilient, and there is sufficient thermal energy to allow for localized molecular rotation and slipping. In this region, the modulus falls off rapidly as secondary intermolecular forces are overcome. In the plateau region, the modulus changes little with temperature, and there are still

significant molecular entanglements, while local sections are very mobile. In the flow region, molecular interactions have less energy than the thermal energy applied and significant slippage occurs. Bouldin et al., (1991) mentioned that G′(ω) plot could be subdivided into four zones: a terminal or flow zone, a plateau zone (only present in case of network), a transition zone and a glassy zone.

Bonemazzi et al., (1996) suggested that rheological tests should be used to predict PMA performances and correlated rheological data like G^*, tan δ, G′, G″ with performance as follows:

- High G^* at high temperature → resistance to permanent deformation.
- Small tan δ at high temperatures → elastic response.
- Temperature independent modulus → low temperature susceptibility.
- High G'' at low temperatures → low-temperature flexibility.

Goodrich (1991 & 1988) stated that dynamic analysis allows one to fingerprint the viscous and the elastic nature of asphalt over a wide range of temperatures and loading times. Rheological properties were correlated with asphalt concrete mixture. In another work, Stastna et al., (2003 and 1999) obtained a viscoelastic model for PMA by using DMA. Again, molecular weight distribution of regular asphalt was studied by DMA and compared this value with GPC (Zanzotto et al., 1999). No significant difference was reported. Jin et al., (2002) used DMA to study PS modified asphalt through vulcanization.

2.5. Master Curve (Time-Temperature Superposition)

Several empirical methods have been developed for predicting the temperature dependence and shear rate dependence of the shear viscosity of a polymer melt from a limited amount of experimental data. Carreau et al., (2000) mentioned that the most important aspect of the rheological properties of asphalts is their dependence on temperature. The behavior of modified asphalt becomes more and more like a viscous fluid with increasing temperature. The basis of time-temperature superposition is to shift data obtained at different temperatures to a certain reference temperature. Construction of the master curves of dynamic material functions is the safest method to characterize conventional and polymer modified bitumens (Zanzotto et al., 2000).

The shift factor is defined by $a_T = \frac{\omega(T_0)}{\omega(T)}$ and is same in the linear as well as non-linear region. In case of many polymers, shift factor is independent of molecular weight. For superposition, well known Williams, Landel and Ferry (WLF). equation is used.

$$\log a_T = \log \frac{\eta_0(T)}{\eta_0(T_R)} = \frac{-C_1(T - T_R)}{C_2 + (T - T_R)} \tag{2.4.1}$$

C_1 and C_2 are constants and $T_R \geq T_g + 100^oC$ where T_g is the glass transition temperature. In case of temperature dependence, the following relation may be used to calculate shift factor:

$$\log a_T = \frac{E}{2.303R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \tag{2.4.2}$$

where, E is the flow activation energy and is calculated from Arrhenius equation, R is the universal gas constant, T is the current temperature and T_0 is the reference temperature.

2.6. Temperature Dependent Viscosity

At temperatures far above T_g or T_m for crystalline polymers, there is ample free volume available, and energy barriers to motion determine the temperature dependence of the zero-shear viscosity. Under these circumstances, the viscosity follows the Andrade or Arrhenius equation to a good approximation:

$$\eta = A\, e^{Ea/RT} \qquad (2.5.1)$$

Where, A is a constant characteristic of the polymer and its molecular weight, E_a is flow activation energy, R is universal gas constant and T is temperature (K).

The presence of polymer in the asphalt mixture results in an increase or decrease of the activation energy. It depends on the type of action between polymer and asphalt phase. Moreover, the physical significance of this parameter still not clearly understood, it has been found to depend on a number of molecular characteristics such as molecular weight distribution, degree of branching, and the nature of the monomer unit. The slight increase of E observed for most polymer concentrations indicates that, within this range of temperature changes, the modified asphalt is more temperature sensitive than the unmodified asphalt (Ait-Kadi et al., 1996). The goal for polymer modification is to reduce temperature sensitivity of base asphalt as properties of a viscoelastic material varies with temperature.

2.7. Asphalt Polymer Blending Requirements

Blends of polymeric materials with asphalt binders are complex. For any specific asphalt binder, the physical properties of the asphalt-polymer blend are affected by the

amount of polymeric material added, its composition, and its M_w. However, the most important factor may be the compatibility of the asphalt with the polymer.

Modifiers are usually supplied in different forms. These are mainly supplied as powder or dust (fillers) form, pellets or granules form, fibers and liquid form (at high concentration in drums or tankers). Each modifier has its own way of mixing and handling. It depends on the modifier type and the purpose of usage. For each modifier, the method of mixing and handling is known either from experience or from supplier recommendations (Terrel and Epps, 1989).

Blending Mechanism: Blending of asphalt binders with high M_w materials, such as polymers, is not a steady and easy operation since two heterogeneous materials are forced together to form a two phase system. The polymer is required to disperse and not to dissolve in the base asphalt binder. Therefore, it is recommended that the blender is capable of providing high shear rate. The configuration of the blender head (i.e., the blade) and the speed of blending define the level of shear rate that the blender induces into the asphalt binder. To ensure that high shear blending is obtained, the recommended speed should not be less than 2500 rpm (Al-Dubabe et al, 1998).

Blending Time: It depends greatly on the blending shear rate and blending temperature. It was found that prolonged blending time besides being uneconomical is detrimental to the rheological properties of the modified binder (Brule et al. 1988). Since blending time depends on the blender configuration and polymer type, it is recommended to identify the optimum blending time for a specific polymer type, blender head configuration and speed by monitoring the increase in the consistency of the PMA by measuring the G″ at uniform time intervals during the blending process (say every 20

minutes or less). Once the G″ stabilizes and does not show a significant increase with time, the blending process can be stopped. A plot of the blending time and G″, such as that shown in Figure 2.5 can be generated, from which the optimum blending time can be determined (Al-Dubabe et. al, 1998).

Blending Temperature: The blending temperature greatly depends on the M_w of the polymer. Higher M_w polymers require higher temperatures than lower M_w polymers (Al-Dubabe et al, 1998).

Blending Temperature: The blending temperature greatly depends on the M_w of the polymer. Higher M_w polymers require higher temperatures than lower M_w polymers (Al-Dubabe et al, 1998).

2.8. Characterization of PMA

(a) Conventional Method: The specification is based solely on traditional tests and includes softening point, viscosity (at 135^{o}C & 180^{o}C), elastic recovery (at 25^{o}C by using ductilometer), storage stability (penetration point, softening point), flash point and test after thin film oven test (softening point, viscosity at 180^{o}C, elastic recovery). These measurements are not sufficient to describe properly the linear viscoelastic and failure properties that are needed to relate bitumen properties to mixture properties. Also the reliability of traditional tests is often questionable.

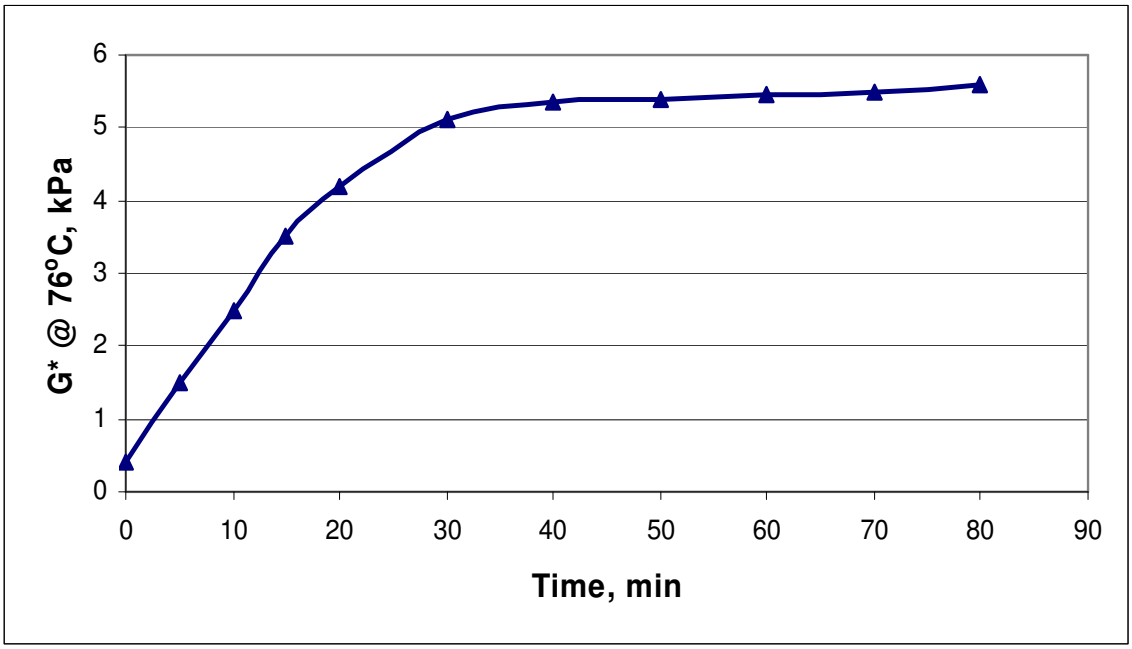


Figure 2.4: Determination of optimum blending time of typical asphalt using G* (Hussein et al., 2004).

(b) Strategic Highway Research Program (SHRP): In SHRP, new powerful tools for the evaluation of bituminous The SHRP system of classification and characterization of asphalt binders put the emphasis on the rheological methods to replace the conventional tests of asphalts (usually have no theoretical background). As asphalt behavior depends on loading time and temperature (a viscoelastic fluid), SHRP has chosen the dynamic shear rheometer as a tool to measure this dependency (Bahia and Anderton, 1995). The criteria adopted by SHRP for an asphalt binder is the highest temperature at which the ratio of G*/ sin (δ) is superior to 1 kPa. This test is used instead of the softening point test.

To evaluate the workability of the asphalt binder, G*/sin δ at the designated temperature and 10 rad/sec frequency is used to evaluate the contribution of the asphalt binder to rutting. Also G*×sin δ is used to evaluate the contribution of the asphalt to fatigue cracking, and creep stiffness, S (60s), and the logarithmic creep rate, m (60s), are used to evaluate low-temperature cracking.

2.9. Cost Effectiveness

Another important factor that needs to be investigated and evaluated in modifying asphalt binders with polymeric materials is the economics. Many laboratory trials have justified the use of polymers to improve the properties of asphalt binders, but practical implementation has always been faced with the increased cost of doing so (Denning and Carswell, 1981).

It is evident from the above discussion and description of the previous efforts in the field of asphalt binder polymer modification that little work has been done within the

Gulf countries to investigate the utilization of polymers as rheology modifiers of asphalt. Moreover, asphalt binders have not been designed for specific use in pavement construction even though they have many interesting properties. Asphalt temperature susceptibility and variable rheological performance, too soft at high temperature and too brittle at low temperature, lead to increasing interest in modifying asphalt binders for specific locations and environments. This interest is expected to grow due to the harsh weather conditions and due to the availability of polymers in Saudi Arabia. Therefore, the major goal in asphalt modification is to find or design a polymer that improves asphalt properties to a satisfactory level at a minimum cost.

Chapter 3

EXPERIMENTAL DESIGN

3.1. Introduction

All works have been divided into two phases. In the first phase, different polymers were blended with asphalt binder and found out the improvement of asphalt binder performance, by comparing polymer modified asphalt binder with base asphalt. In the second phase, base asphalt as well as polymer modified asphalt was mixed with concretes to perform water sensitivity, Marshall Stability, resilient modulus and rutting test.

3.2. Materials

Six different types of polymer resins were used. These polymers can be categorized into 3 types, low density polyethylene (LDPE), ethyl vinyl acetate (EVA) and acrylate. LDPE and EVA polymers were supplied by Exxon Mobil. Acrylate polymers were obtained from DuPont. Table 3.1 showed the characterization data like melting point, melt index of the resins, which are provided by the suppliers. Also, molecular weight and molecular weight distribution (MWD) are show in Table 3.1. These data were

Table 3.1**:** Characterization data of the polymer resins

Commercial Name	**Polymer Type**	**Melting point (^oC)**	**Density (g/cm^3)**	**Melt Index (g/10min)**	**M_w (kg/mol)**	**MWD**
LD 655	LDPE	100	0.913	155	71.92	9.75
LD 654	LDPE	100	0.913	70	102.92	12.4
UL 15028 CC	EVA	68	0.95	150	30.48	5.3
UL 15019 CC	EVA	81	0.938	150	35.62	4.71
Elvaloy 3427AC	Acrylate	94	0.926	4	80.43	4.23
Elvaloy 4170	Acrylate	52	0.576	8	90.76	5.61

*UL 15028CC contains 27.5 wt% VA

*UL 15019CC contains 19 wt% VA

*Elvaloy 3427AC contains 27% butyl acrylate

*Elvaloy 4170 contians > 99% ethyl acrylate

by gel permeation chromatography (GPC). Asphalt binder was collected from Riyadh Refinery. The aggregates, which were used for asphalt aggregates mix tests, were collected from Al-Dossary Asphalt Plant.

3.3. Polymer Asphalt Modification

3.3.1. Blender

A blender was used to blend asphalt with the polymers. Three different weights (4 wt%, 6 wt%, and 8 wt %) of each polymer were blended with asphalt. In a small container, asphalt was heated to 160^{o}C in an oil bath to control the temperature. At this temperature, asphalt was almost liquid like and polymers were in melt state to ensure better mixing. A certain percentage of polymers were added in the container. A DC motor was used to control the blending speed up to 2400 rpm. Figure 3.1 shows the schematic diagram of the blending machine and its accessories.

3.3.2. Rheological Measurement

To measure the rheological properties, sample was prepared in a disk shape. The disk was inserted between the Advanced Rheometrics Expansion system (ARES) rheometer platens, pre-heated in mounted position within the ARES oven, to achieve the intended working temperature as measured with a thermocouple embedded in the lower platen and contacting the melt during the testing procedure. Figure 3.2 shows the ARES rheometer and schematic of parallel palte geometry. With the sample in position, the oven was closed and the sample was heated for 2 minutes, the upper platen force transducer assembly was lowered to the proper working position.

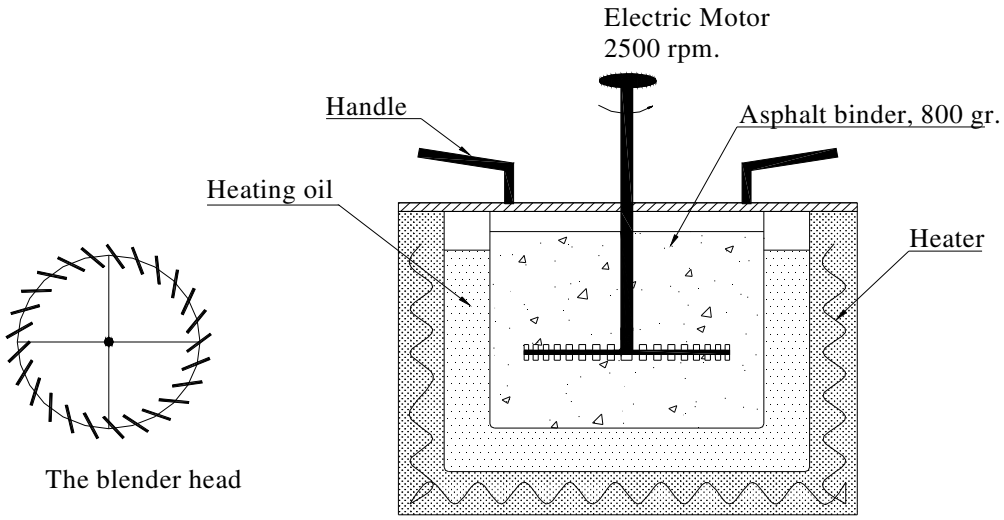
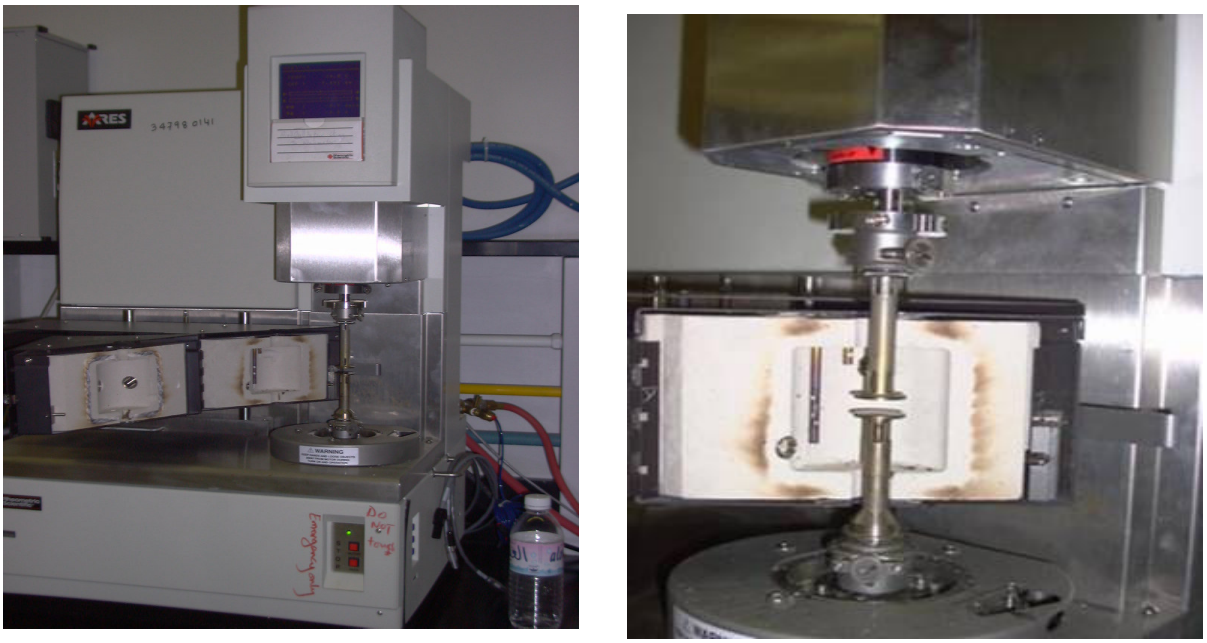
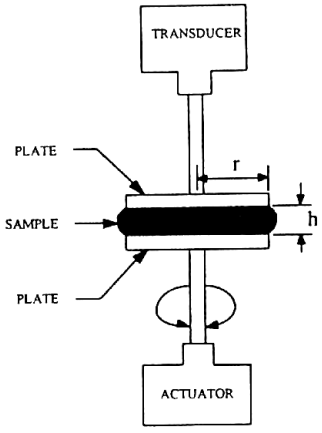


Figure 3.1: Schematic representation of blending machines



(a)



(b)

Figure 3.2: (a) Advanced Rheometrics Expansion System (ARES) Rheometer;

(b)Schematic diagram of parallel plate geometry

With the system at operating temperature and the nitrogen blanket in place, a holding period of 2 minutes was allowed for thermal equilibrium before beginning measurements.

All rheological measurements was performed using ARES rheometer, where different dynamic shear tests was done. Time sweep tests assessed rheological properties over a long period of time at constant temperature; strain and frequency were carried out to study the thermal stability of the melts.

3.3.3. Storage Stability

The storage stability of asphalt binders was tested as follows. After blending about 800 ml samples at optimum blending time, the container was placed in an oil bath for continuous agitation. The temperature of this bath was 160^{o}C and the agitation was continued for 72 hours at 500 rpm. Figure 3.3 shows the schematic diagrams. After 72 hours, the samples were collected form top and bottom of the container by a pipette. The storage stability of the modified asphalt binders were evaluated according to the Laboratory Asphalt Stability (LAST) procedure (Bahia et al., 2001).

3.3.4. Rolling Thin Film Oven (RTFO)

The RTFO test was used to simulate the aging that takes place during the production and up to the first life of the pavement. The base asphalt as well as modified asphalt was poured into cylindrical bottles. Then bottle were placed horizontally in a convection oven, which was rotated at 163^{o}C for 85 min. This process created a thin film of asphalt on the inside of the bottles. Figure 3.4 shows the photograph of rolling thin film oven.

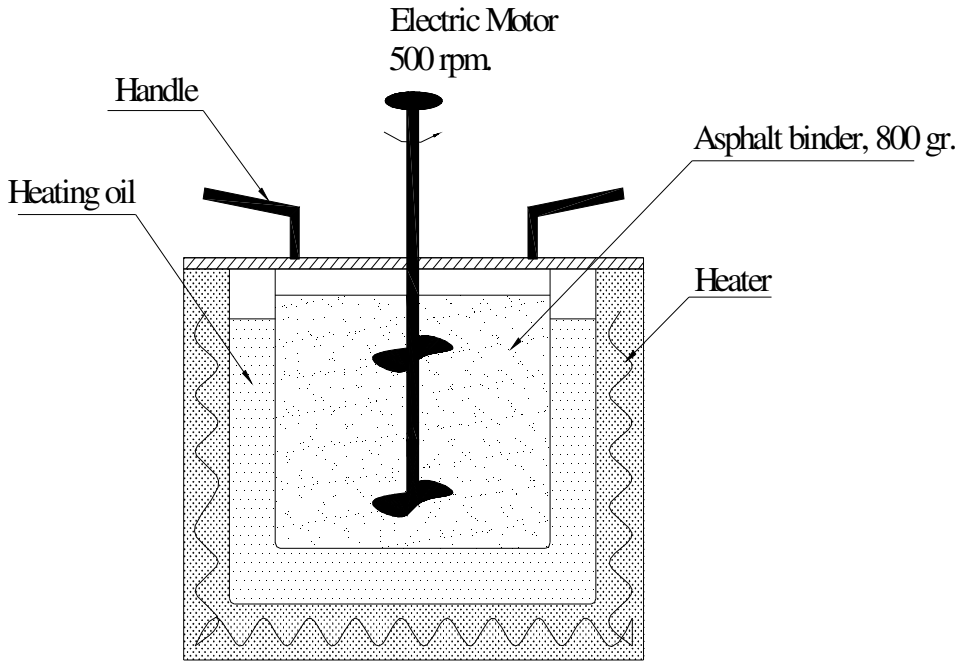


Figure 3.3: Schematic diagram of storage stability equipment

Figure 3.4: Rolling Thin Film Oven (RTFO)

3.3.5. Pressure Ageing Vessel (PAV)

The next step in the simulation of the ageing process for the binder was the pressure ageing vessel. The RTFO aged binder was placed in shallow pans approximately 3 mm thick. During the PAV process, oxygen was driven into the binder. It simulates long term ageing of the binder in the pavement. Figure 3.6 shows the photograph of pressure aging vessel.

3.3.6. Bending Beam Rheometer (BBR)

BBR will be used to measure the low temperature stiffness properties of a binder. In the test, a beam of asphalt will be subjected to a three point loading in a low temperature bath at 10^{o}C above the above the expected low pavement temperature. Figure 3.6 shows the photograph of BBR test machine.

3.4. Asphalt Concrete Mix

Table 3.2 shows the details of asphalt concrete mix design. The design was obtained according to Marshall Mix design method. Both asphalt concrete mix (ACM) and polymer modified asphalt concrete mix (PMACM) were prepared for the wearing course at the optimum asphalt content. The standard Marshall specimen of 100 mm × 62.5 mm were prepared for the following tests.

3.4.1. Marshall Stability test

Marshall Stability test of ACM and PMACM was obtained as follows: six specimens were immersed in a water bath at 60^{o}C. After 40 minutes, three specimens were used to determine the maximum applied testing load by Marshall Testing Machine,

Figure 3.5: Pressure Ageing Vessel (PAV)

.

Figure 3.6: Bending Beam Rheometer (BBR)

Table 3.2: Mix Design

	Job Mix Formula (JMF)	**Specification Limits**
1. Optimum Asphalt Content, % (60/70 Pen grade asphalt)	5.3	5.3 +/- 0.3
2. Aggregate Grading: % Passing		
1"	100	100
3/4"	87	80 - 95
# 4	55	48 - 62
# 10	38	32 - 45
# 40	21	16 - 26
# 80	13	8 - 18
# 200	6	4 - 8
3. Marshall Test Results (75 blows, compaction temperature 150^{o}C)		
Stability (Kg)	1804	800 Min.
% Air Voids. Total Mix	4.4	4.0 - 6.0
Flow (mm)	3.2	2.0 - 4.0
% Voids filled w/asphalt	74	70 - 80
Stability Loss, (%)	16.2	20 Max.
Void in Mineral Aggregates (VMA)	16.04	-

a compression testing device, which is designed to apply loads to test specimens through semi-circular testing heads at a constant rate of strain of 51 mm (2 in.) per minute, was used. This condition was considered as the initial condition. The remaining three specimens were kept for 24 hours in the water bath at the same temperature and were tested later according to the same procedure and named as final condition. The obtained load was multiplied by stability correlation ratio and corrected load was calculated.

3.4.2. Water Sensitivity test (Lottman test, AATO T-283-89)

Three specimens were put in a water bath at room temperature for 2 hours; specimens from the water bath were then placed between the two bearing plates in the test machine. Care was taken to apply the load along the diameter of the specimen. The load (indirect tensile strain, ITS) was applied on the specimen at a constant deformation rate of 51 mm per minute and the load at failure was obtained. Three more specimens were placed in a container and a vacuum of 20 in Hg for 4 minutes was applied. Then specimens were kept in a water bath at 60^{o}C for 24 hours. After that, they were put in another water bath at room temperature for 2 hours and indirect tensile strength (ITS) was measured. The average difference in ITS due to conditioning was obtained.

3.4.3. Resilient Modulus

It is the measure of pavement response in terms of dynamic stresses and corresponding strains. A static load of about 10 lb was applied to hold the specimen in place. A repeated load in the linear range was applied with a frequency of 1 Hz. and the resulting horizontal deformation was obtained at 50^{o}C.

3.4.4. Permanent Deformation (Rutting) test

Permanent deformation measurements were performed on ACM and PMACM at 50^{o}C. The load was used for 150 initial μ-strain deformations. Deformation due to applied repeated load was obtained until the failure of the specimen. The permanent deformation was measured by linear variable differential transducer and data was stored in a data logger. Data were collected at every 5 s for the first 100 load repetitions, and every 10 s for the next 100 repetitions. Then every 15 s for the following 100 repetitions finally every 30 s until the specimen fails. Linear region results were analyzed to compare the accumulated deformation due to repeated load among ACM and PMACM.

Chapter 4

RESULTS AND DISCUSSION

4.1. Influence of Mw of LDPE and Vinyl Acetate Content of EVA on the Rheology of Polymer Modified Asphalt

(Rheologica Acta, in press)

4.1.1. Abstract

Asphalt binder was modified by low density polyethylene (LDPE) and ethyl vinyl acetate (EVA) polymers to investigate the structure-property relationships of polymer modified asphalt (PMA). The PMA was prepared in a high shear blender at 160^{o}C. The optimum blending time (OBT) for each polymer was determined following a separate investigation. OBT was influenced by Mw, MWD, and polymer structure. The influence of Mw of LDPE and vinyl acetate (VA) content of EVA on PMAs was studied by rheological tools. Polymer modification improved the rheological properties of base asphalt. EVA PMAs were found to be less temperature sensitive than LDPE modified asphalts. LDPE modification increased flow activation energy (E_a) but EVA modification decreased E_a. Both VA content and Mw of LDPE have influenced the storage stability of PMAs. The low temperature properties of PMAs and short ageing tests were not influenced by polymer type. On the other hand, the high temperature properties of PMAs

were strongly influenced by Mw of LDPE and VA content of EVA. Overall, EVA with low VA content showed the best temperature resistance to high temperature deformations, the highest upper service temperature as well as the best storage stability.

4.1.2. Introduction

Asphalt is used as road carpeting material throughout the world. Because of the availability of relatively low cost binders, the roadway networks in the Gulf Countries have developed rapidly more than those of many other industrialized countries (Al-Dubabe et al., 1998). The increase in road traffic during the last two decades in combination with an insufficient degree of maintenance has caused an accelerated deterioration of road structures in many countries (Isacsson and Lu, 1995; Lu and Isacsson, 1997). To minimize the deterioration and thereby to increase the long term durability of a flexible pavement, the asphalt layers should be improved with regard to performance related properties, such as resistance to permanent deformation, low temperature cracking, load-associated fatigue, wear, stripping and ageing. Moreover, for certain applications, such as bridges, runways and surfaces with high traffic loading, special binders are urgently required (Lu and Isacsson, 1997).

Asphalt modification with different materials was done in the past (Lu and Isacsson, 1997; Zanzotto et al., 1996; Bouldin et al., 1991; Muncy et al., 1987; Goodrich 1988). Recently, a large number of investigations showed that asphalt properties (e.g., viscoelasticity and temperature susceptibility) can be improved by using an additives or a chemical modification for high temperature as well as low temperature applications (Isacsson and Zheng, 1998; Lu and Isacsson, 2001; Lu et al., 1998; Fawcett et al.; 2000, Johansson and Isacsson, 1998; Nair et al., 1998; Collins et al., 1991; Bahia and Davis,

1994; Bonemazzi et al., 1996; Blanko et al., 1996; Adedeji et al., 1996; Ali et al., 1999; Wen et al., 2002). Among the different types of additives, polymers are the most promising modifiers. Although there are many polymers, only few are suitable for asphalt modification (Lu and Isacsson, 2001). These polymers should resist the degradation at asphalt mixing temperatures (about 160^{o}C) and maintain their premium properties during storage and application (Varma et al., 2002; Sabbagh and Lesser, 1998; Rozeveld et al., 1997). Also, the polymer should be compatible with asphalt; capable of being processed with conventional mixing/laying equipment, and cost effective (Garcia-Morales et al., 2004; Gao et al., 2002; Lu et al., 1999). To achieve the goal of improving asphalt properties, the selected polymer should create a secondary network or a new balanced system within asphalt by molecular interaction. The formation of a functional modified binder system is based on the dissolution and/or fine dispersion of polymer in asphalt and on the compatibility of the polymer/asphalt system.

In addition to the influence of polymer molecular parameters, there is a significant effect of blending time and temperature on PMA. Long blending time causes structural damages of asphalt (Yousefi 2003; Al-Dubabe et al., 1998). Further, high shear rates disintegrate polymers and reduce their sizes to micrometer and submicrometer scales in asphalt medium. This will inhibit polymer entanglement with asphalt phase. Blending time can be selected by measuring the softening point after a certain time interval at the time of blending (Al-Dubabe et al., 1998).

In this study, the influence of Mw of low density polyethylene (LDPE), VA content of EVA as well as polymer type and polymer concentration on asphalt modification was investigated. Two polymers that are widely used in asphalt

modification namely, polyethylene and EVA were selected. The influence of Mw (or Melt Flow Index, MFI) of the polymer was examined by using two LDPE samples of the same density but of different MFIs. The influence of VA content on asphalt modification was investigated by selecting two EVA resins of similar MFI and of different VA content. Also, a comparison of LDPE and EVA (of almost similar MFI) would reveal the influence of polymer type. Here, the influences of these parameters, such as M_w (or MFI) and VA content or structural parameters (LDPE vs. EVA) were studied one parameter at a time. Also, most of the previous work was performed in cold climates (Canada and Sweden) where improvement of the low temperature performance of PMAs was of great concern. For Saudi Arabia (and other hot climates in the world), the high temperature performance of PMA is important for PMAs. Here, the high temperature performance of PMAs is emphasized. This study is part of a research plan aiming at selecting a proper type of polymer that could be used for polymer modification of local asphalt. The plan involves testing the PMA concrete mixes, too. In this paper, the PMAs of LDPE and EVA are studied.

4.1.3. Experimental

Materials

2 LDPEs and 2 EVAs were used in this study. All are commercial polymers and were supplied by ExxonMobil. Table 4.1.1 provides characterization data such as density, MFI at 190^{o}C/2.16 kg and melting point as provided by ExxonMobil. The number-average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) were obtained by a gel permeation chromatography (GPC). GPC data was obtained by using 1,2,4 trichlorobenzene as solvent at 150^{o}C in a WATER

GPC2000 instrument. Polystyrene standards were used for calibration. Branch content was obtained for LDPE polymer by NMR and it was 18.8 and 18.2 CH_3/1000C for LDPE1 and LDPE2, respectively. On the other hand, the VA content of the EVA samples was 19 wt% and 27.5 wt%, respectively. The VA content was provided by the supplier and the ratio was confirmed by NMR. The low M_w LDPE and the low VA content EVA were denoted by label 1, where the high M_w LDPE and the high VA content EVA were assigned the label 2.

Asphalt of 60/70 penetration grade was used in this study. This asphalt was obtained from Saudi Aramco Riyadh Refinery. The weight percentage of C, H, S and N content of asphalt was obtained by elemental analysis as 85.70%, 10.26, 3.90% and 0.4%, respectively. To determine the amount of the heavy fractions in asphalt (asphaltenes), it was dissolved in toluene and 0.45-μm filter was used for filtration (El-Mubarak et al., 1999). According to this gravimetric method, asphalt, used in this study, was found to contain 30% asphaltenes.

Determination of Optimum Blending Time (OBT)

To avoid long blending time, the OBT for the 8% concentration was obtained. Complex shear modulus ($|G^*|$) at 76°C was used to monitor the consistency of PMA during blending. The temperature of 76°C was selected since it represents the highest performance grading requirements in the Gulf countries (Al-Dubabe et al., 1998). $|G^*|$ was measured for samples collected during the blending at 5, 10, 15, 20, 25, 30, 40 and 50 minutes of the start of the blending process. The OBT was determined as the time needed for $|G^*|$ (or torque) to reach steady state. The steady state was defined as the first plateau of torque-time curve. Prolonged heating is believed to be behind the increase

Table 4.1.1: Characterization of polymers

Polymer	**Density (g/cm^3)**	**MFI (g/10min)**	**Melting Point, ^oC**	**M_n (kg/mol)**	**M_w (kg/mol)**	**M_w/M_n**
LDPE1	0.913	155	100	7.376	71.920	9.7
LDPE2	0.913	70	100	8.304	102.929	12.4
EVA1	0.938	150	81	7.566	35.629	4.7
EVA2	0.95	150	68	5.757	30.486	5.3

in torque following the plateau as a result of x-linking (Yousefi, 2003). For all other parts of this study, all PMA samples were prepared at the OBT obtained for the 8% polymer concentration.

PMA Sample Preparation

800 g of asphalt were heated at 160^{o}C for 50 minutes. Oil bath was used to control the temperature. Pre-weighed polymer was poured in the asphalt. A special blender composed of high shear blade (Al-Dubabe et al., 1998) was used to blend the polymer with the asphalt; the blending speed was controlled with a DC motor capable of producing up to 3000 rpm. Three different polymer concentrations (4%, 6% and 8 wt %) were used. After blending at the OBT, samples were collected in a rubber mould of 25 mm diameter and 2 mm thickness and tested within 24 hrs.

Polymer Specimen Preparation

Before rheological testing, as received polymers were given a controlled thermomechanical history (molding) in a Carver press. 25 mm diameter and 2 mm thick polymer flat discs were prepared. Molding was conducted according to the melting point of polymer. Polymer pellets were charged between the platens of the press under 3 metric tons of pressure for 1 min. Then, pressure was increased to 5 metric tons and held for 1 min. Thereafter, pellets were kept for 5 min at 7 metric tons pressure. Finally, water was used to cool the platens to room temperature and discs were collected for rheological testing.

Rheological Characterization

All rheological tests of pure asphalt as well as polymers and PMAs were carried out in a strain controlled ARES rheometer. Parallel plate geometry with a diameter of 25 mm and a gap of 1.5 mm was used in all of these studies. This is mainly due to the fact that cone-and-plate geometry was not used for temperature sweeps to avoid metal-metal contact. Strain sweep tests were performed on PMAs and base asphalt to check for the linear viscoelastic range and 20% strain amplitude was selected. All tests were conducted under nitrogen environment to avoid any possible degradation. Reproducibility tests were performed on the 4% LDPE1 PMA to check for any possible degradation in PMA (Hussein et al., 2000). The samples were obtained from two different batches. The results of reproducibility tests are given in Figure 4.1.1. The agreement of both viscous and elastic properties shows the excellent reproducibility of these measurements. The frequency sweep was carried out at 76^{o}C in the range 100 to 0.1 rad/s. Temperature sweep test was done over the temperature range 50^{o}-100^{o}C at 5^{o}C/min ramp rate (to avoid long exposure time at high temperature) and a frequency ω=10 rad/s. Also, frequency-temperature sweep tests were performed to construct time-temperature superposition (TTS) curve. In that case, the temperature range covered was 50-90^{o}C at a step of 10^{o}C. In all temperature sweep tests, 2.5 microns/^{o}C were used as tool thermal expansion coefficient following a separate calibration experiment.

Storage Stability Test

The tests aim at assessing the storage stability of PMA, which is related to the miscibility of asphalt-polymer blend. The storage stability of asphalt binders was

performed as follows: after blending 800 g of asphalt sample at OBT, the container was placed in an oil bath at 160^{o}C for continuous agitation at 500 rpm. After 72 hours, the samples were collected from the top and the bottom of the container by a pipette. The storage stability of the modified asphalt binders was evaluated according to the Laboratory of Asphalt Stability Test (LAST) procedure (Bahia et al., 2001). G* values at 76^{o}C and 10 rad/s were measured in ARES rheometer for the top and the bottom samples. Then, the difference was calculated. This test helps in assessing the miscibility of polymer-asphalt blend, which is critical for storage and final use of PMA.

Rolling Thin Film Oven (RTFO) Test

RTFO was used to perform ageing of asphalt binders according to ASTM D 2872 procedure. This test simulates the ageing process that takes place during the production and up to the first year of the service life of the pavement. After blending, asphalt binder was poured into cylindrical bottles, placed horizontally in a convection oven and rotated at 163^{o}C for 85 minutes. Air was supplied into the bottle to accelerate ageing. A thin film was created on asphalt. After completing the run, samples were collected for rheological testing in ARES.

Performance Grading (PG)

PG of PMAs was done for all samples with a 4% polymer concentration. The steps of the PG are as follows: residue from RTFO was placed in a Pressure Aging Vessel (PAV) where temperature was held at 110^{o}C and oxygen was supplied continuously following Strategic Highway Research Program (SHRP) B-005 test procedure. After 20 hours, samples were collected from the PAV for measurement of $|G^*|$. According to SHRP, the upper limit of PG represents the temperature at which

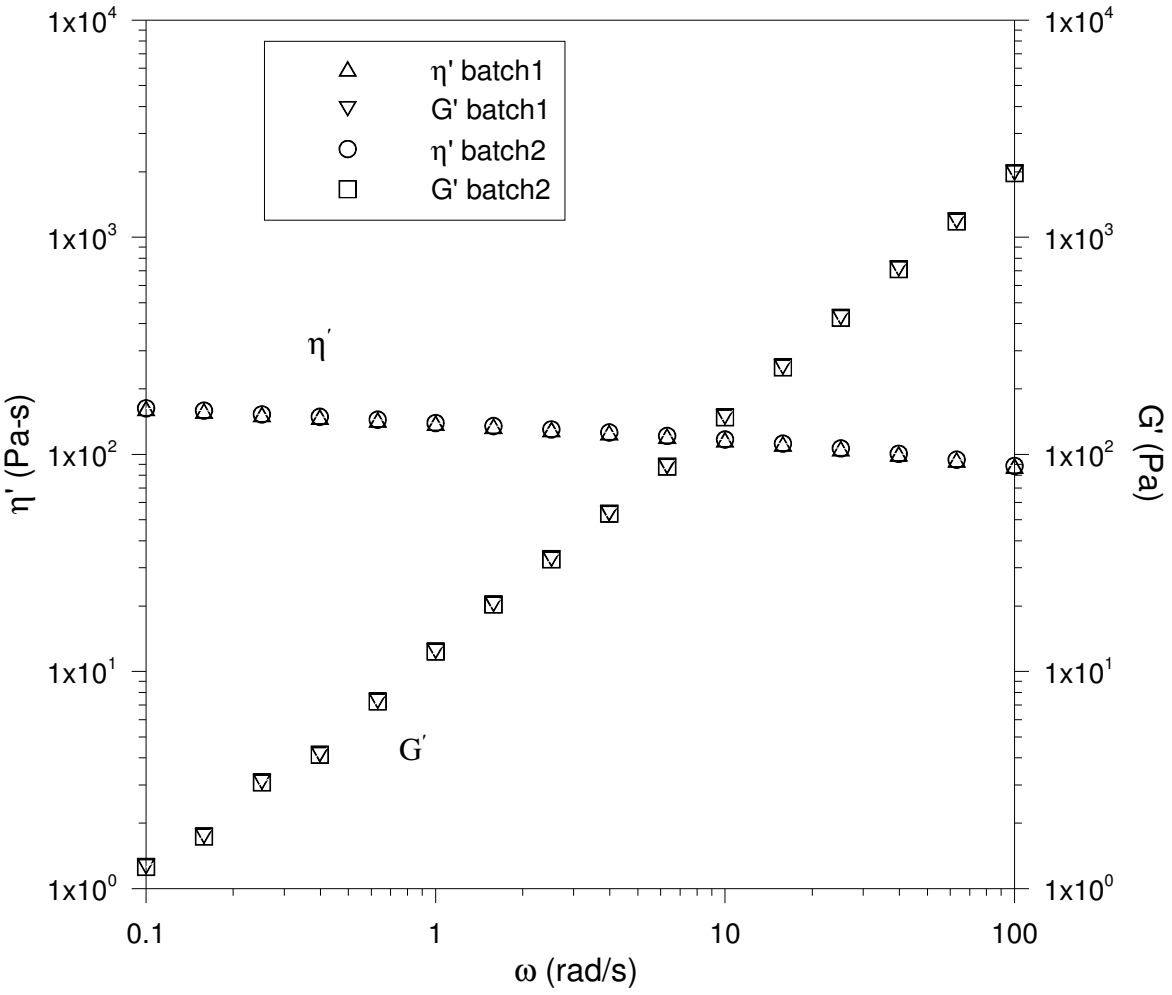


Figure 4.1.1: Batch reproducibility test, $\eta'(\omega)$ and $G'(\omega)$ for 4% LDPE1 and asphalt blend. (T=76°C, γ^o = 20%).

$|G^*|/\sin\delta$ is at least 1 kPa. Also, beams (12.4 cm×1.2 cm×0.6 cm) were prepared to find the lower temperature limit of PG using a Fisher's Bending Beam Rheometer (BBR).

4.1.4. Results and Discussion

Optimum Blending Time

The values of $|G^*|$ are shown in Figure 4.1.2 for all PMAs. Base asphalt was treated under the same conditions. The diamond, upper triangle, lower triangle, circle and square symbols represent base asphalt, LDPE1, LDPE2, EVA1 and EVA2 PMAs, respectively. $|G^*|$ value of asphalt was smaller than 1 kPa (SHRP minimum requirement) over the whole time range; however, polymer modification increased $|G^*|$. Initially, $|G^*|$ increased rapidly and then the rate of increase slowed down with time. The minimum time required by $|G^*|$ (torque) to attain at the steady state is taken as the OBT. It should be noted that after the first plateau increase in torque was observed, which is likely due to x-linking as a result of prolonged heating. OBTs of 8% LDPE1, 8% LDPE2, 8% EVA1 and 8% EVA2 PMAs were 30, 20, 15 and 20 minutes, respectively. EVA1 PMA showed rapid initial increase in $|G^*|$, while EVA2 PMA showed the least initial increase. The initial behavior of OBT curve of the LDPE modified asphalt was similar. However, LDPE2 (low MFI, high Mw) reached the steady state faster than LDPE1 (high MFI, low Mw), while the reverse was expected.

Although MFI characterizes the thermoplastic polymers, the rheological behavior of a polymer at high shear rate indicates the degree of mixing with asphalt. This can be clearly explained by power law model. Low power-law index polymer gives more shear thinning behavior at high shear rate and need less time for dispersion. So, knowledge of

MFI of polymers is not sufficient since the shear thinning behavior is significant, too. Frequency sweep tests of pure polymers were performed and the value of power law indices (n) were 0.73, 0.63, 0.72 and 0.85 for LDPE1, LDPE2, EVA1 and EVA2 polymer, respectively. It can be seen that LDPE2 exhibits more shear thinning behavior and its power low index is less than LDPE1. So, it has a low viscosity at high shear rate and LDPE2 takes less time to attain steady state in the high shear blender. Also, GPC analysis (Table 4.1.1) showed higher PDI for LDPE2 (the high Mw polymer) in comparison with LDPE1 (the low Mw resin). This explains the shear thinning behavior of LDPE2 and the low OBT. In the case of EVA polymer, this explanation was quite clear. Both EVA polymers have the same MFI but their shear thinning behavior is different. For EVA2, n value is high so the PMA took more time to reach in steady state.

Rheological Analysis

The comparison of asphalt and PMAs are presented in Figure 4.1.3, which reports the dynamic viscosity (η') at 76^{o}C as a function of ω. In this case, the 4% concentration of different polymers was taken. The base asphalt showed typical Newtonian behavior over almost the whole ω-range with a zero shear viscosity, η_o, of 95.485 Pa-s. Similar observations were reported in the literature (Zupancic and Zumer, 2002; Bahia and Davies, 1994). Addition of 4% of a polymer has increased η' of PMAs at low-ω. However, the results depend on the type of the polymer. EVA1 PMA showed the highest increase in viscosity at low frequency region. EVA2 modified asphalt showed a decrease in η' at high-ω. LDPE2 modified asphalt displayed the same viscosity as EVA1 at high-ω. This effect is quite clear in Figure 41.4, where $|G^*|$ was plotted as a function of phase angle (δ). This diagram was generated with frequency sweep data.

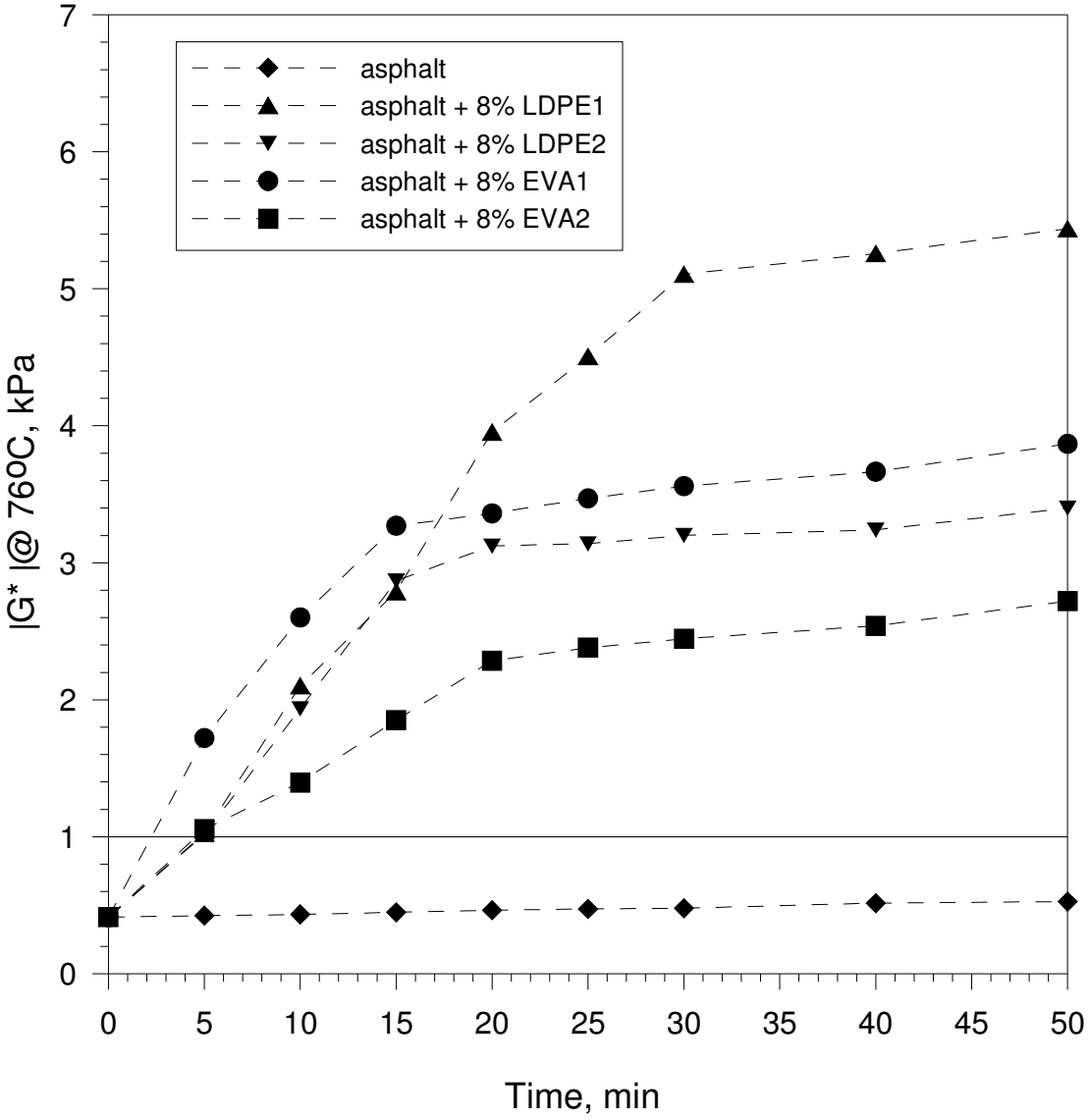


Figure 4.1.2: Blending time determination.

PMA showed substantial decrease in δ (increase in elastic response) with decreasing $|G^*|$ compared to base asphalt. Both EVA PMAs is found to decrease more in comparison to LDPE PMAs. The effect of polymer concentration on $\eta'(\omega)$ (filled symbol) and $G'(\omega)$ (open symbol) of LDPE1 is shown in Figure 4.1.5 for the three different polymer concentrations. It was observed that both rheological properties of modified asphalt increased with the increase of polymer content, which is expected.

The effect of polymer concentration on $\eta'(T)$ was studied by performing temperature sweeps on LDPE1 PMA at three different polymer concentrations. The results are shown in Figure 4.1.6. At high temperatures (~90^{o}C), the 8% LDPE1 PMA showed a sudden decrease in η' values. High polymer concentrations result in PMA with higher elasticity; however, the blend has the tendency to phase separate. Phase separation was suggested for PMA with more than 7 wt% polymer concentration (Brule, 1996). However, high temperature would weaken the interfacial tension between the dispersed LDPE1 phase and the asphalt continuous phase. This would result in improvement of the blend miscibility and hence reduce the viscosity of the blend (Hameed and Hussein, 2002). The observed drop of the 8% LDPE1 PMA viscosity at high temperature supports the existence of a multiphase system at lower temperatures since Arrhenius behavior was not followed. In fact, at these low temperatures LDPE1 is below its melting point (see Table 4.1.1) and it is a semisolid in a matrix of asphalt melt which justifies the multiphase explanation.

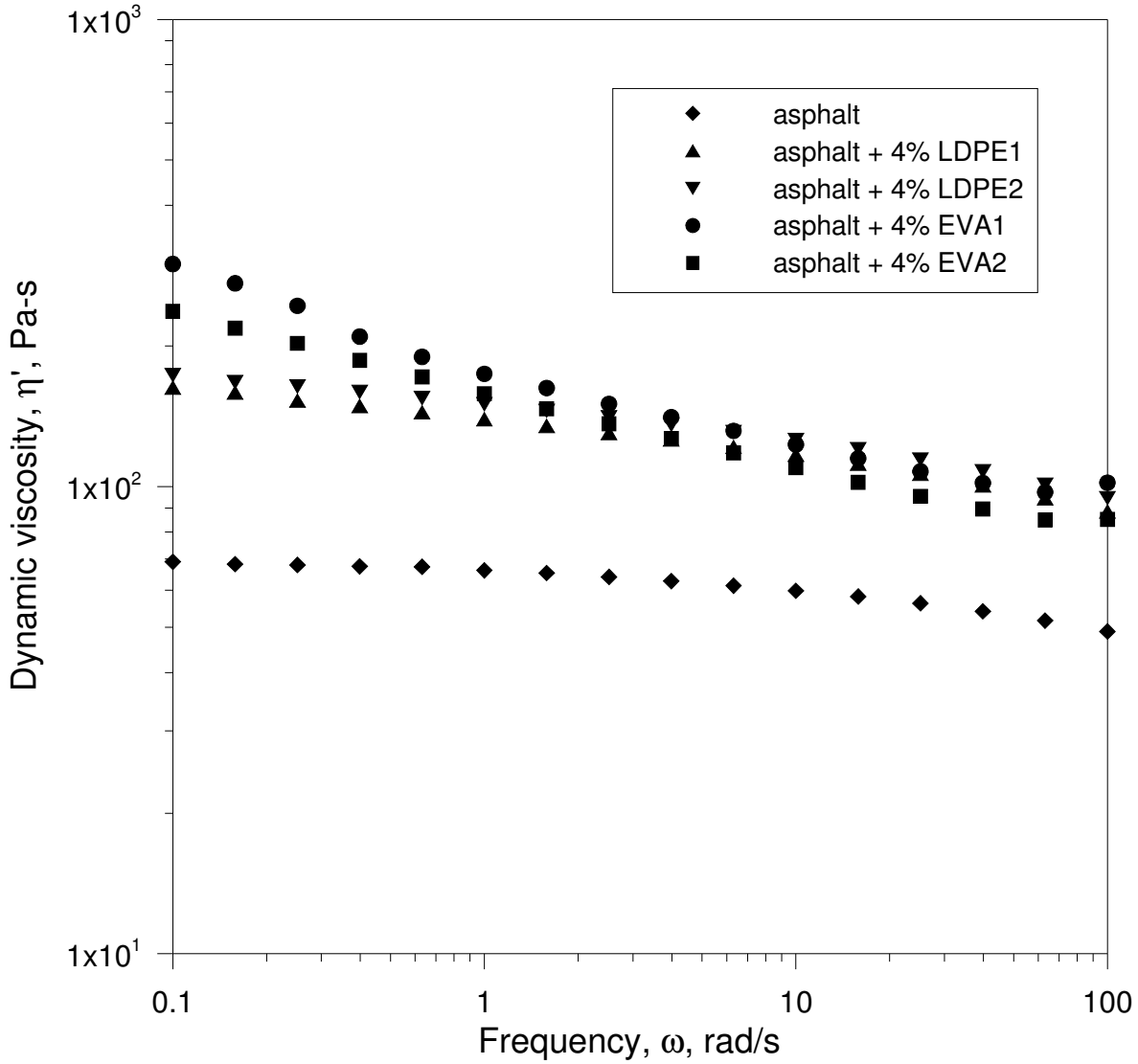


Figure 4.1.3: η′ (ω) of the asphalt and polymer modified asphalts at 76°C (γ^o = 20%).

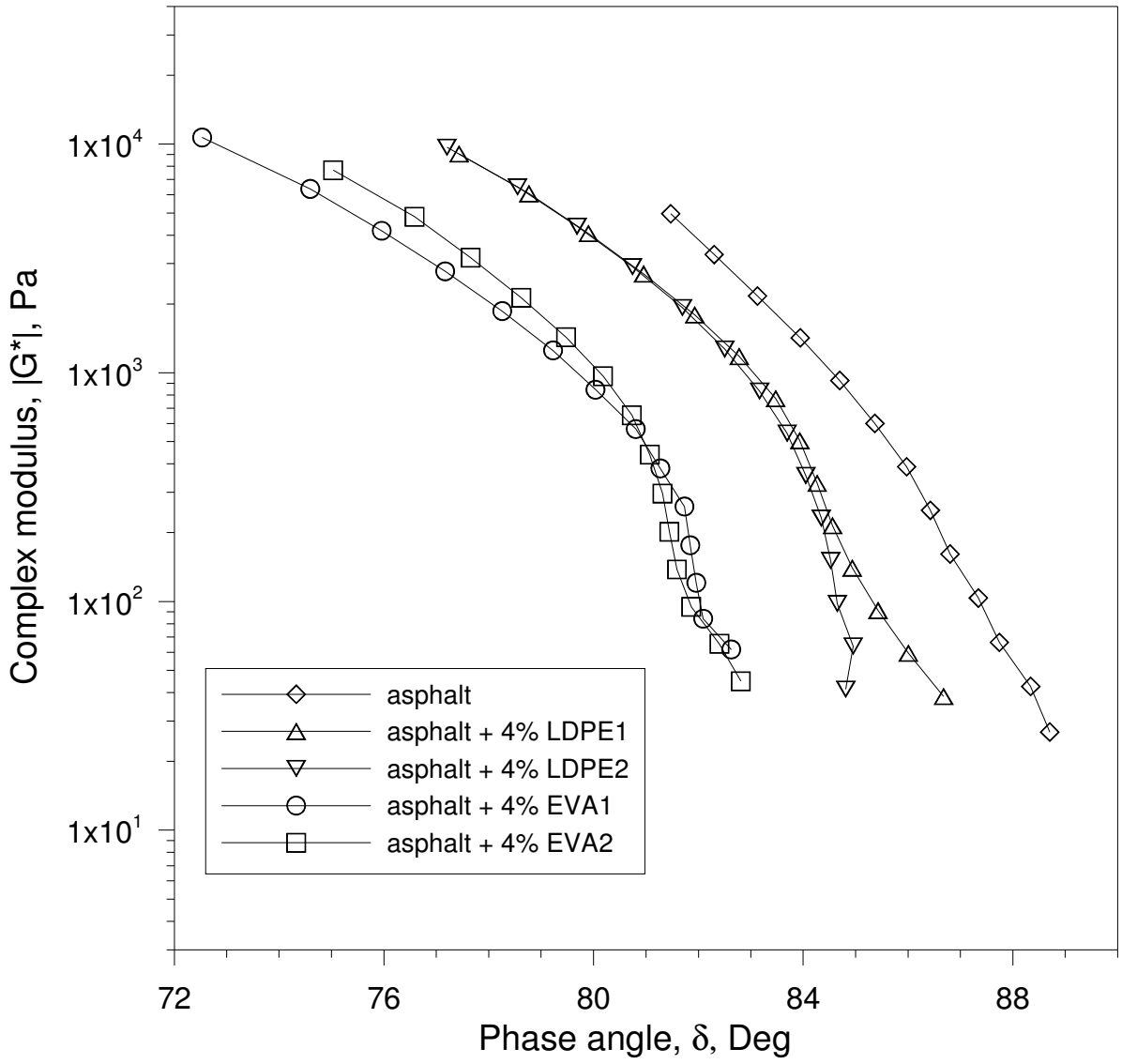


Figure 4.1.4: G* as a function of δ. (T = 76°C).

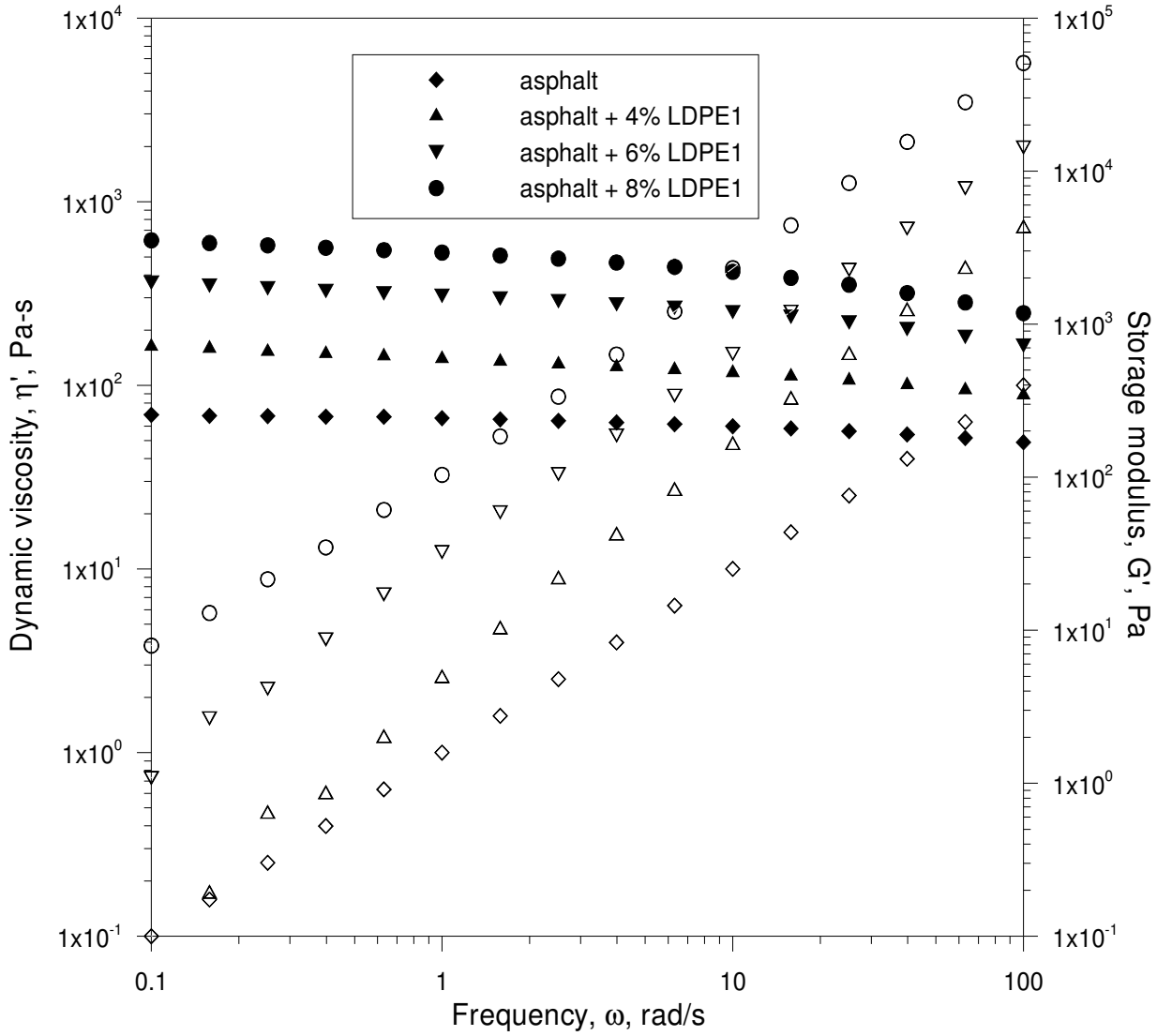


Figure 4.1.5: Effect of polymer concentration on $\eta'(\omega)$ and $G'(\omega)$ at 76°C (γ^o = 20%).

Temperature sweep tests were also used to obtain flow activation energy from well known Arrehenius equation.

$$\eta^* = A\, e^{Ea/RT} \qquad (4.1.1)$$

where A is pre-exponential term, E_a is activation energy, T is temperature and R is universal constant. Table 4.1.2 shows the values of flow activation energy (E_a) and the pre-exponent (A) of modified asphalt for three different polymer concentrations of each polymer. E_a increased when LDPE was used. Flow activation energy increased with the increase of LDPE concentration. This behavior of LDPE modified asphalt is similar to previous observations of different researchers (Zupancic and Zumer, 2002; Carreau et al., 2000; Ait-kadi et al., 1996). On the other hand, EVA modified asphalt decreased the flow activation energy significantly and lower E_a values were obtained at higher polymer content. Low activation energies are preferred since they result in lowering the change of viscosity with the change of temperature. Both EVA1 and EVA2 polymers showed similar behavior with regard to the influence of polymer content on E_a. This behavior is likely due to the rigid nature of the

EVA molecule (double bond in the backbone). Here, we would like to offer tentative explanations. The high VA content EVA2 is likely to act as a rigid molecule that reinforces the flexible asphalt matrix, while EVA1 acts as a flexible polymer chain that entangles with asphalt molecules. Higher VA content is likely to reduce the degree of entanglement of polymer asphalt molecules. So, it seems like low VA content would allow the polymer molecule to entangle with asphalt; hence increase the elasticity of PMA. However, high VA content would likely render the polymer molecule too stiff and reduce the entanglement density of polymer-asphalt micelles. Here, we are excluding any

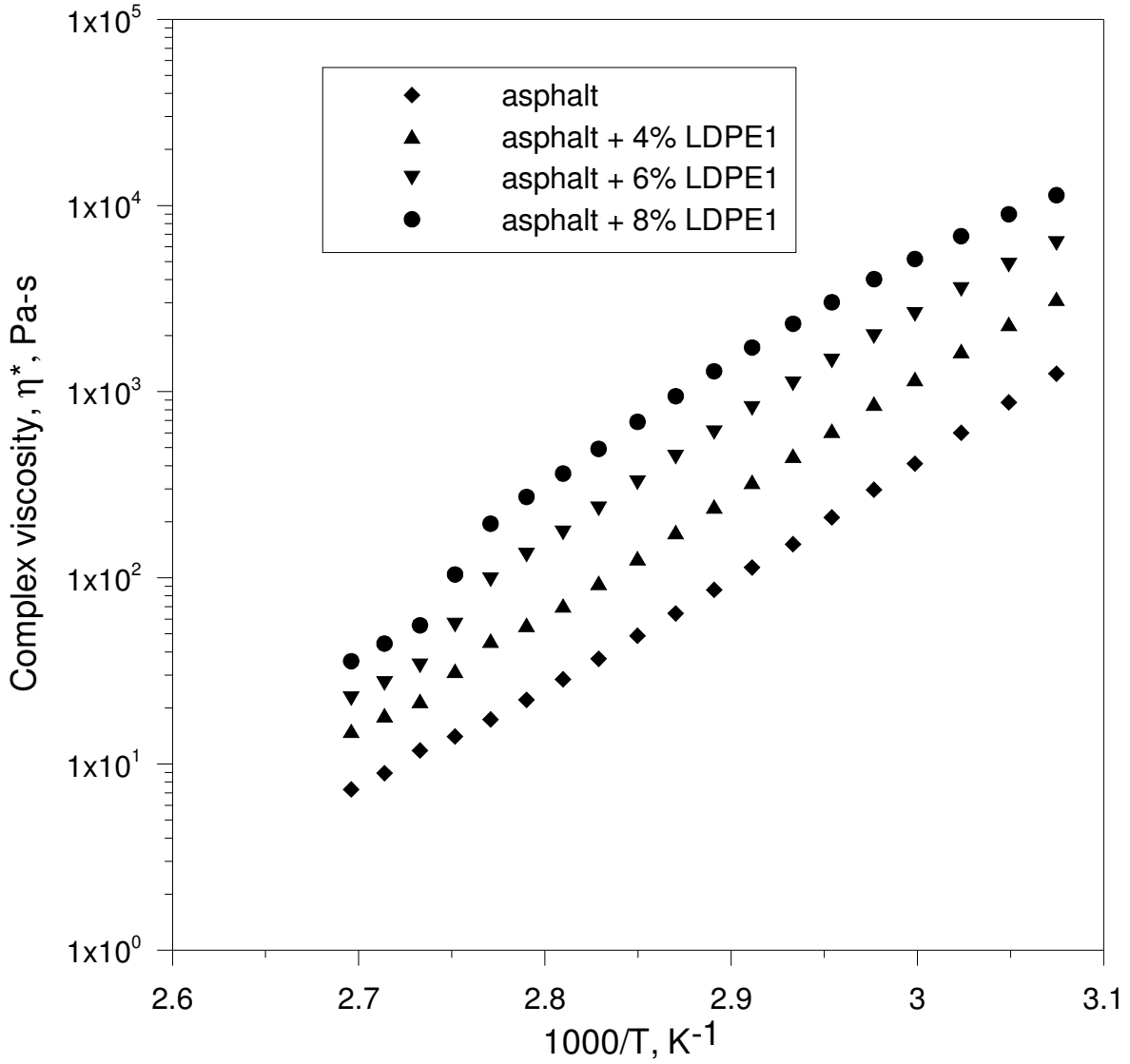


Figure 4.1.6: Effect of polymer concentration on η*(T) (ω = 10 rad/s, γ^o = 20%).

Table 4.1.2: Comparison of Arrhenius parameters for modified asphalt

Material type	**Polymer wt%**	**A (Pa-s)**	**E_a (kJ/mol)**	**η* (Pa-s), @ 50°C**	**η*(Pa-s), @ 60°C**	**% Difference**
asphalt	0	5.00E-16	114	1.34E+03	3.75E+02	72.01
LDPE1	4%	3.00E-16	118.47	4.24E+03	1.13E+03	73.35
	6%	7.00E-17	124.86	1.07E+04	2.65E+03	75.23
	8%	6.00E-17	127.27	2.24E+04	5.41E+03	75.48
LDPE2	4%	3.00E-16	118.94	5.05E+03	1.34E+03	73.46
	6%	1.00E-16	122.96	7.52E+03	1.90E+03	74.73
	8%	1.00E-16	124.93	1.57E+04	3.88E+03	75.28
EVA1	4%	9.00E-14	101.97	2.74E+03	8.76E+02	68.03
	6%	3.00E-13	99.89	4.21E+03	1.38E+03	67.22
	8%	8.00E-12	91.78	5.48E+03	1.99E+03	63.68
EVA2	4%	1.00E-13	100.2	1.57E+03	5.14E+02	67.26
	6%	6.00E-12	90.04	2.15E+03	7.87E+02	63.40
	8%	4.00E-12	91.18	2.58E+03	9.93E+02	61.62

other explanations based on chemical reaction. This is mainly due to the fact that blending of EVA polymers with asphalt for long times (50 min) in the high shear blender did not produce significant increase in the elasticity of PMA. Still the polymers used in this part of the study were blended at much less time (see optimum blending time part). Also, $|G^*|$ for asphalt was stable over a long period of time (see the OBT curve). Hence, these polymer modifications are dominated by physical rather than chemical interactions.

The percent decrease in viscosity of PMA due to the increase in temperature from 50°C to 60°C was calculated by Arrhenius equation and results are shown in Table 4.1.2. These temperatures were selected because about this temperature range asphalt goes to Newtonian region (Polacco et. al., 2003). It was observed that the difference was high for LDPE polymers and the difference has increased with the increase of polymer concentration. But EVA polymers showed less decrease in viscosity when temperature was increased from 50°C to 60°C. This decrease in viscosity is even less at high EVA concentrations.

As PMA is a viscoelastic material, it exhibits non-Newtonian behavior over wide temperature range and cannot be defined only by zero-shear viscosity (Singh et. al., 2003; Zupancic and Zumer, 2002; Carreau et. al., 2000). Time-temperature superposition (TTS) is used to explain this behavior. For TTS, Williams-Landel-Ferry (WLF) equation is used.

$$\log a_T = \log \frac{\eta_0(T)}{\eta_0(T_R)} = \frac{-C_1(T - T_R)}{C_2 + (T - T_R)} \tag{4.1.2}$$

where, C_1 and C_2 are constants and $T_R \geq T_g+100^oC$ and T_g is the glass transition temperature. Figure 4.1.7 shows the elastic modulus (G′) as a function of reduced frequency (ωa_T) obtained from temperature-frequency sweeps. Data are presented for the 4 % polymer concentration systems. The reference temperature was 70^oC. The temperature dependence of the shift factor, a_T, is given in Figure 4.1.8**.** Similar behavior was reported in the literature (Zupancic and Zumer, 2002; Carreau et al., 2000, Challa et al., 1996, 1997; Chebil et al., 1996). It is observed that time-temperature superposition (TTS) principle holds for all materials over the experimental range of temperatures and frequencies.

The fact that the four PMAs covered in this study follow TTS suggests that the polymer-asphalt blend is miscible. At low ω, EVA1 PMA showed the highest G′ among all polymers. LDPE modified asphalt displayed higher elasticity in comparison to base asphalt. In the high-ω range, the effect of polymer type was not pronounced. The low-ω (long time) range reflects the high temperature behavior of PMA. This suggests that EVA1 of low VA content would show higher modulus at high temperature, which is preferred for hot climates. These results are in agreement with the previous findings from Figure 4.1.3. The high VA content polymer (EVA2) displayed the lowest modulus among the four polymers. Hence, EVA1 of low VA content is expected to have the best high temperature resistance to permanent deformations (rutting).

At low-ω, the slopes of base asphalt, LDPE1 and EVA1 PMAs were found to be 1.2, 0.92 and 0.73, respectively. Since these slopes were obtained in the low-ω range (corresponds to high temperature according to TTS), the elastic properties of EVA1 are expected to be less temperature sensitive compared to other polymers.

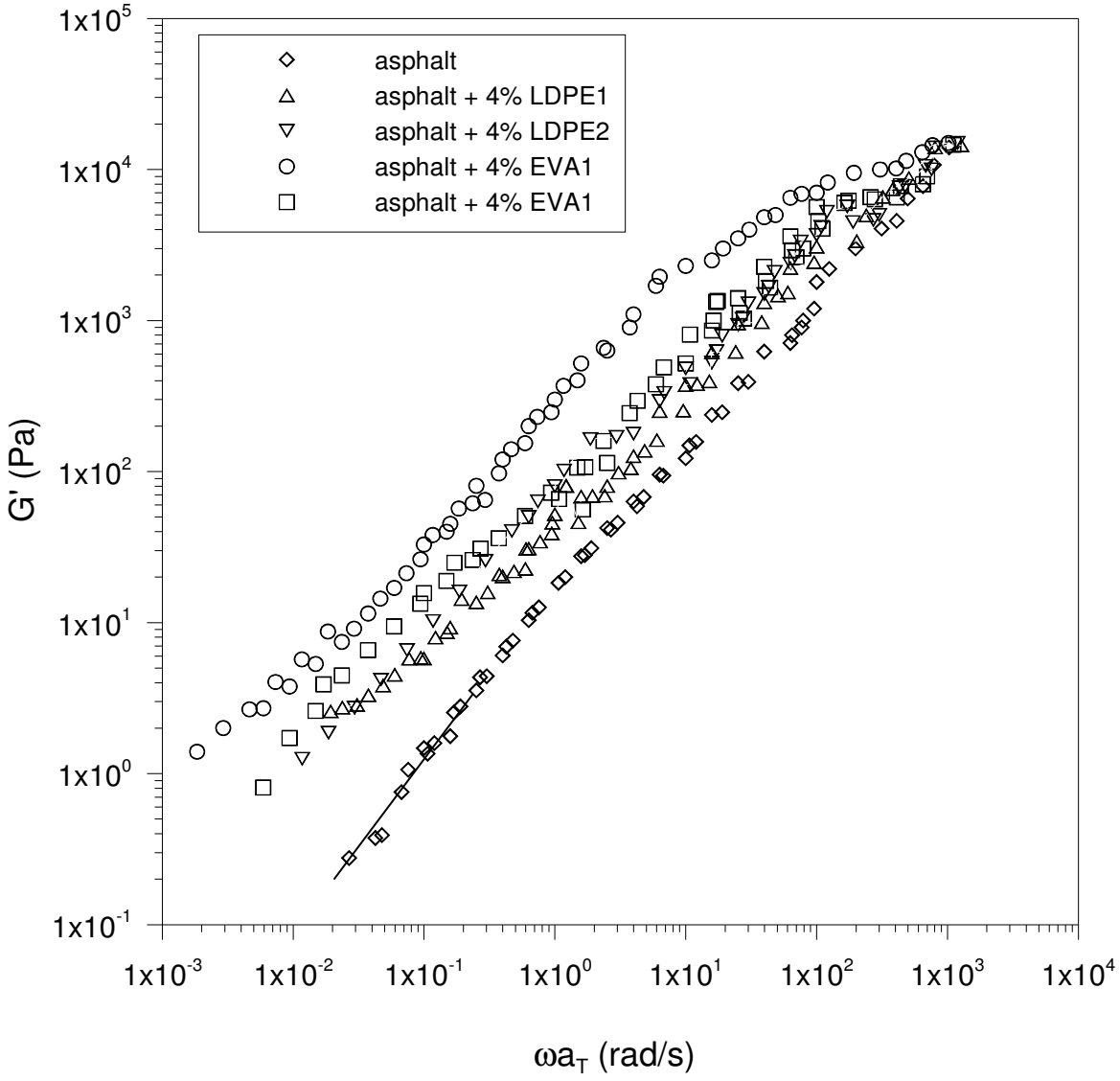


Figure 4.1.7: G′(ω) master curve for all polymer modified asphalt at T_{ref}=70°C.

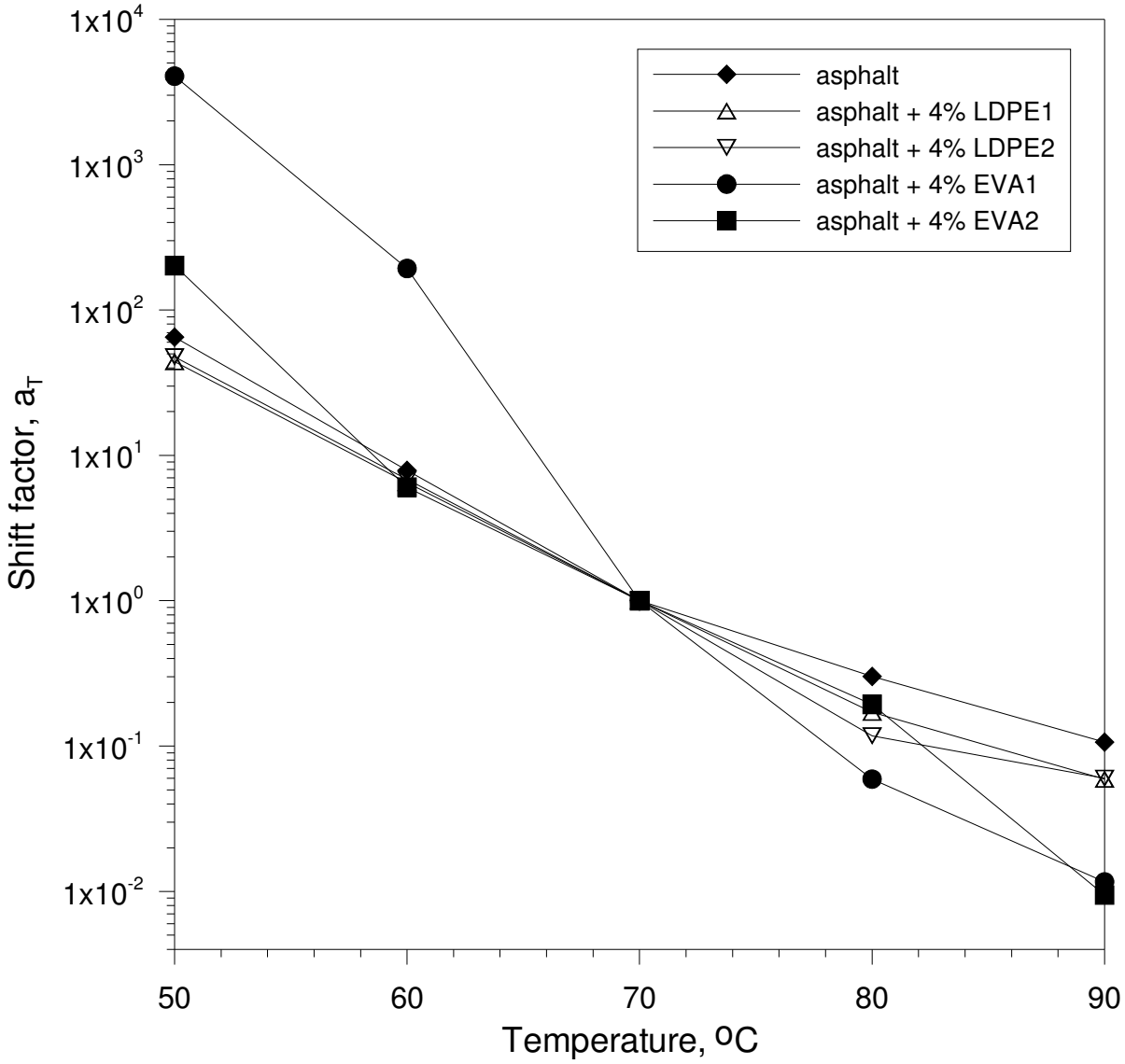


Figure 4.1.8**:** a_T vs. T (T_{ref} = 70°C).

Accordingly, EVA1 PMA is expected to show better performance in rutting resistance. Hence, the information extracted from the slopes of G′ vs. ω is consistent with the above findings obtained from the comparison of G′ data. To improve the rutting resistance of PMA, higher values of G′ are needed. In the high-ω region (corresponds to low temperature according to TTS), PMAs with high loss modulus (G″) are preferred to prevent crack initiation. However, the low temperature behavior of all of the above polymers approaches similar values at high ω. Therefore, the high temperature performance is the main factor in the selection of the polymer type. This is likely to be applied in hot climates only where temperature sensitivity is important.

According to SHRP method, the asphalt can be used up to that temperature when $|G^*|/\sin\delta$ value is at least 1 kPa. These values are 70°C, 80°C, 80°C, 82°C and 77°C for asphalt, 4% LDPE1, 4% LDPE2, 4% EVA1 and 4% EVA2 PMA, respectively. Polymer modification has improved the service temperature according to SHRP specification. Among all polymers, EVA1 gave the highest service temperature (82°C) at $|G^*|/\sin\delta=1$ kPa. Moreover, the 4% polymer concentration of all polymers satisfies the high service temperature requirement for the Gulf region (76°C). So, further analysis was performed on the PMA with only 4% polymer concentration.

Storage Stability Test

Structurally, asphalt is very complex (Stastna et al., 2003; Gao et al., 2002; Rassamdana et al., 1996). It is composed of different phases. Addition of polymer enhances this complexity. Always there is a possibility of phase separation during storage at elevated temperature. 4% of all polymers were used and showed $|G^*|$ values that are

high at the top and the bottom after 72 hrs. The high temperature and long mixing time would result in considerable oxidation that would eventually lead to the observed increase in $|G^*|$. The bottom sample showed higher values of $|G^*|$ than that of the top. The percent differences between top and bottom value of $|G^*|$ are 9, 3, 5 and 18 for LDPE1, LDPE2, EVA1 and EVA2 PMAs, respectively. This phase separation was the highest for EVA2 and the least for LDPE2. Further, in the comparison of LDPE1 and EVA1, EVA1 showed better storage stability than LDPE1, which supports the previous observations on the phase separation of the 8% LDPE. EVA1 (low VA content) showed better storage stability than EVA2 (high VA content). EVA2 is more rigid as it contains more VA than EVA1 and it is not compatible with asphalt. Isacsson and Lu (1999) concluded that high vinyl acetate (VA) content leads to poor storage stability. However, the ethyl vinyl acetate (EVA) polymers used in that study were of different molecular weights. So, it is difficult to conclude whether that observation was due to the influence of molecular weight (Mw) or VA content. Also, the fact that EVA2 showed more phase separation supports our tentative explanation that the rigid EVA2 has less entanglement with asphalt and is just reinforcing the asphalt matrix phase. This finding is in agreement with previous literature reports (Lu et al., 1999). So, EVA with low VA content has the best storage stability compared to other polymers covered in this study.

Rolling Thin Film Oven (RTFO) Test

Figure 4.1.9 and Figure 4.1.10 show $\eta^*(T)$ value of base asphalt and 4% PMAs before and after treatment in the RTFO test. Ageing has increased the complex viscosity without much influence on the flow activation energy (almost similar slope). The values

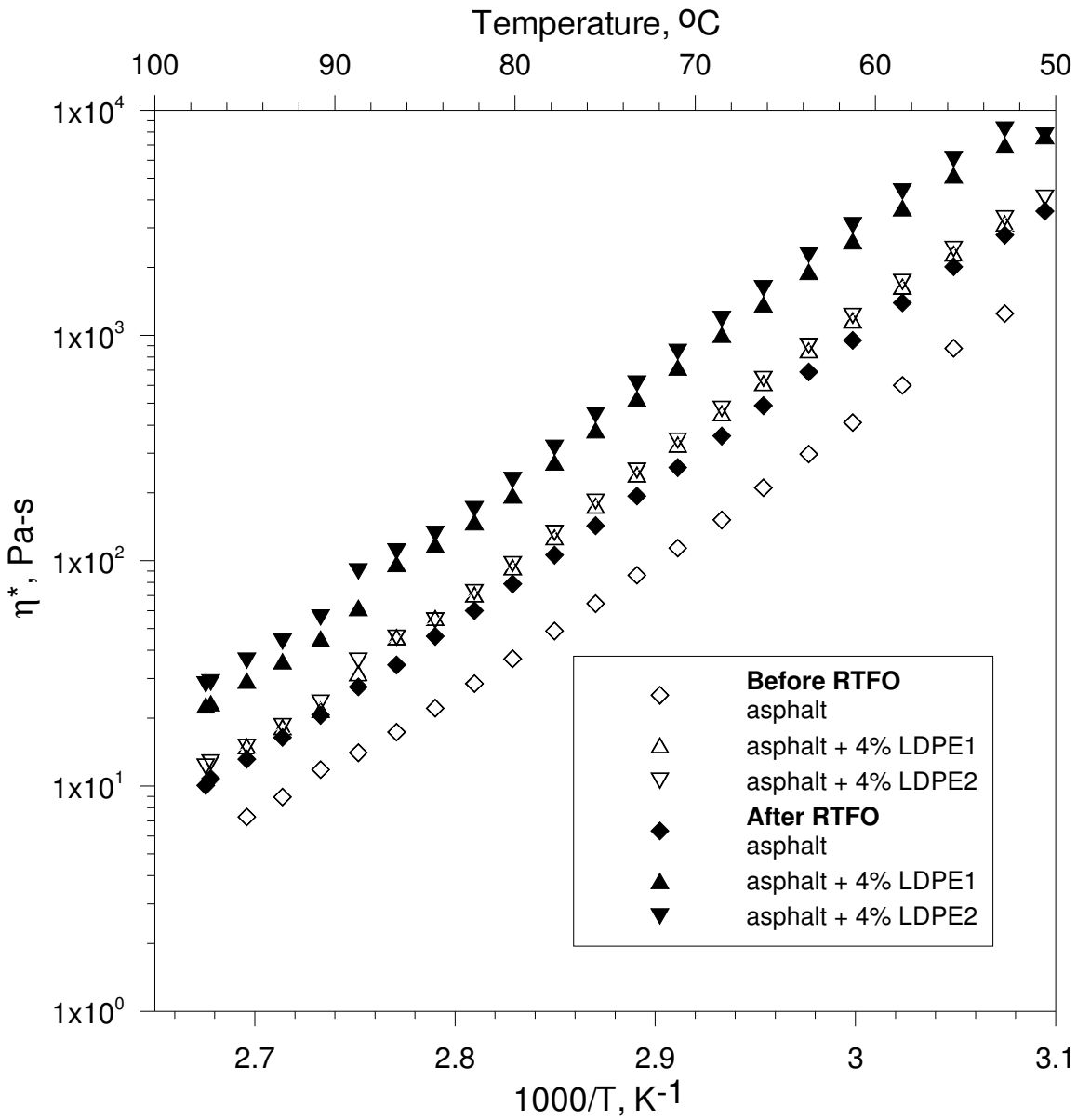


Figure 4.1.9: Effect of LDPE on the asphalt binder ageing (ω = 10 rad/s, γ^o = 20%).

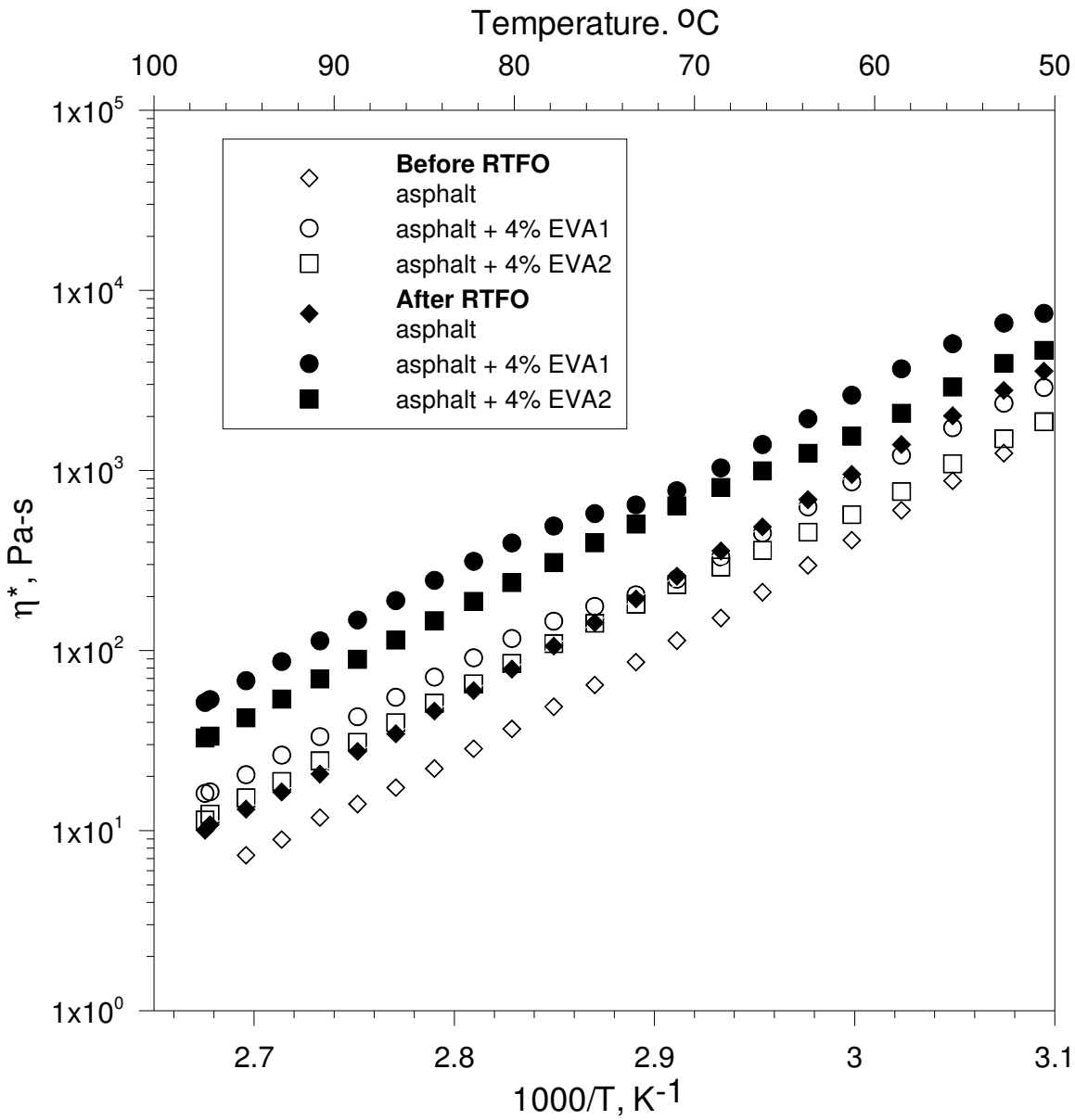


Figure 4.1.10**:** Effect of EVA on asphalt binder ageing (ω = 10 rad/s, γ^o = 20%).

of viscoelastic properties of aged specimens were generally higher than those of unaged samples. It is quite similar to the physics of ageing processes that involve x-linking. Temperature ageing favors the volatilization of low molecular weight constituents of asphalt. But high molecular weight constituents remain in the asphalt. Both oxidation and volatilization of asphalt lead to the observed increase in η*. A look at Figures 9 and 10 suggests that both the Mw of LDPE and the VA content of EVA did not show a strong influence on the results of the RTFO test over this short ageing period (85 minutes).

Performance Grading

According to SHRP, the highest PG in the Kingdom is 76-10. PG for asphalt, 4% LDPE1, 4% LDPE2, 4% EVA1 and 4% EVA2 are 64-22, 76-16, 76-10, 82-10 and 76-16, respectively. EVA1 modified asphalt showed the highest service temperature. Other PMA systems have satisfied the required upper limit service temperature of 76^{o}C. Moreover, all PMAs with 4% polymer concentration satisfied the lower limit of -10^{o}C.

4.1.5. Conclusion

The influence of Mw of LDPE and the vinyl acetate content of EVA on modification of asphalt were investigated. Optimum blending time for EVA modified asphalt was found to be lower than that of LDPE modified asphalt due to the difference in Mw. For EVA polymers with similar Mw, higher MWD (or PDI) resulted in shorter blending times in the high shear blender. So, both Mw and MWD as well polymer structure (LDPE1 vs. EVA1) have influenced the OBT.

Polymer modification has significantly enhanced the rheological properties of asphalt. Viscous and elastic properties of modified asphalt increased with the increase of

polymer content. Both EVA polymers decrease the flow activation energy. The reduction of the flow activation energy reduces the degree of temperature sensitivity; hence, reduce the change of viscosity due to temperature change. The VA content of EVA had little or no influence on flow activation energy. The activation energy for LDPE PMAs increased with the increase of polymer concentration, while that of EVA PMAs decreased. This suggests that LDPE PMAs are more temperature sensitive than EVA polymers. Storage stability was found to be acceptable for LDPE and low VA content EVA modified asphalt. However, EVA with high VA content showed the highest degree of phase separation. Also, LDPE of low Mw displayed higher extent of immiscibility with the asphalt used in this study. Comparison of EVA1 (low VA content) and LDPE1 (low Mw) PMAs shows that the storage stability of EVA1 modified asphalts is better.

Both asphalt and PMAs were found to harden due to ageing with no strong influence for Mw or VA content. Both the Mw of LDPE and the VA content of EVA did not show a strong influence on the results of the RTFO test performed over the short ageing period (85 minutes) according to ASTM D 2872 test procedure. The performance grading of the 4% PMAs was carried out and all polymers satisfied the required PG. EVA with low VA content extended the upper service temperature of asphalt by 6^{o}C above the required temperature. On the other hand,

Overall, EVA1 of low VA content has the best high temperature resistance to permanent deformations (rutting) and the highest service temperature as well as the best storage stability (compatibility with asphalt). Both EVA1 and EVA2 polymers showed similar behavior with regard to the influence of polymer content on E_a. Whereas, LDPE of higher Mw showed better compatibility with asphalt and higher elasticity. Otherwise,

the Mw of LDPE showed little or no influence on temperature sensitivity (flow activation energy) or the upper service temperature. Finally, the Mw of LDPE and VA content of EVA have influenced the rheology, the storage stability and the ageing of PMAs differently. Overall, EVA with low VA content was the best asphalt modifier among the polymers covered in this investigation.

4.1.6. References

Adedeji A, Grunfelder T, Bates FS, Macosko C W, Gardiner S M, Newcomb DE (1996) Asphalt Modified by SBS Triblock Copolymer: Structures and Properties. Poly Eng Sci 36(12): 1707-1723.

Ait-Kadi A, Brahimi B, Bousmina M (1996) Polymer Blends for Enhanced Asphalt Binders Polym Eng Sci, 36(12): 1724-1733.

Al-Dubabe IA, Al-Abdul Wahhab HI, Asi IM, Ali MF (1998) Polymer Modification of Arab Asphalt. ASCE Material J 10(3): 161-167.

Ali M, Al-Abdul Wahhab HI, Asi I, Al-Dubabe I (1999) Characterization of Polymer Modified Gulf Asphalts. Petroleum Science and Technology 17(1, 2): 125-146.

Bahia HU, Hanson DI, Zeng M, Zhai H, Khatri MA, Anderson RM (2001) Characterization of Modified Asphalt Binders in Superpave Mix Design. NCHP Report 459, National Academy Press, Washington D.C.

Bahia HU, Davies R (1994) Effect of Crumb Rubber Modifiers on Performance Related Properties of Asphalt Binders. Proc. AAPT 63: 414-450.

Blanko R, Rodriguez R, Garcia-Garduno M, Castano VM (1996) Rheological Properties of Styrene-Butadiene Copolymer-reinforced Asphalt. J Appl Polym Sci 61: 1496-1501.

Bonemazzi F, Braga V, Corrieri R, Giavarini C, Sartori F (1996) Characteristics of Polymers And Polymer-Modified Binders. *TRB*.1535: 36-47.

Bouldin MG, Collins JH, Berker A (1991) Rheology and Microstructure of Polymer/Asphalt Blends. J Rubber Chem & Tech 67(4): 577-600.

Brule B (1996) Polymer Modified Asphalt Cements Used in the Road Construction Industry: Basic Principles. *TRB*1535: 48-53.

Carreau P J, Bousmina M, Bonniot F (2000) "The viscoelastic properties of Polymer-Modified Asphalt. The Canadian J Chemical Eng 78(3): 495-502.

Challa A, Ciochina OG, Roy C, Bousmina M (1997) Rheological Properties of Bitumen Modified with Used Tyre-Derived Pyrolytic Oil Residue. Polym Recycling 3(1): 1-14.

Challa A, Roy C, Ait-kadi A (1996) Rheological Properties of Bitumen Modified with Pyrolytic Carbon Black. Fuel 75(13): 1575-1583.

Chebil S, Challa A, Roy C (1996) Modification of Bitumen with Scrape Tyre Pyrolytic Carbon Black. Comparison with Commercial Carbon Black Part I: Mechanical and Rheological Properties. Polym Recycling 2(4): 257-269.

Collins JH, Bouldin MG (1991) Stability of Straight and Polymer Modified Asphalts, *TRB*. 1342: 92-100.

El-Mubarak AH, Sheikheldin SY, Fayad NM, Khaja N (1999) Development of a Simple Monitoring Technique for Oil pollution in Sediment. J Environ Sci Health A34(2):391-404.

Fawcett AH, McNally TM (2000) A Dynamic Mechanical and Thermal Study of Various Rubber-Bitumen Blends. J Appl Polym Sci 76:586-601.

Fawcett AH, McNally T (2000) Blends of bitumen with various polyolefins. Polymer 41: 5315-5326.

Gao Gt, Zhang Y, Zhang YX, Sun K, Fan YZ (2002) Improved Storage Stability of LDPE/SBS Blends Modified Asphalt. Polym & Polym Comp, 10(3): 229-236.

García-Morales M, Partal P, Navarro F J, Martinez-Boza F, Mackley M R, Gallegos C (2004) The rheology of recycled EVA/LDPE modified bitumen. Rheol Acta in press.

Goodrich J L (1988) Asphalt and Polymer Modified Asphalt Properties Related to the Performance of Asphalt Concrete Mixes. Asphalt Paving Technology, 57: 116-175.

Hameed T, Hussein IA (2002) Rheological Study of the influence of Mw and Comonomer Type on the miscibility of m-LLDPE and LDPE. Polymer, 43: 6911-6929

Hussein IA, Ho K, Goyal SK, Karbashewski E, Williams MC (2000) Thermomechanical Degradation in the Preparation of Polyethylene Blends. Polymer Degradation & Stability 68(3):381-392.

Iqbal MH (2004) Influence of Polymer Type and Structure on the Modification of Saudi Asphalt. MS Thesis (KFUPM).

Isacsson U, Lu X (1999) Laboratory Investigation of Polymer Modified Bitumens. J Association of Asphalt Paving Technol (AAPT) 68: 35-63.

Isacsson U, Zeng H (1998) Cracking of Asphalt at Low Temperature as Related to Bitumen Rheology. J Materials and Structures 33(8):2165-2170.

Isacsson U, Lu X (1995) Testing and Appraisal of Polymer Modified Road Bitumens-State of the Art. Materials and Structures 28: 139-159.

Johansson L S, Isacsson U (1998) Effect of filler on Low Temperature Physical Hardening of Bitumen. Construction and Building Materials 12: 463-470.

Lu X, Isacsson U (2001) Effect of Binder Rheology on the Low-Temperature Cracking of Asphalt Mixtures. Road Materials and Pavement Design 2(1): 29-47.

Lu X, Isacsson U, Ekblad J (1999) Phase Separation of SBS Polymer Modified Bitumens. J Mat Civil Eng 11: 51-57.

Lu X, Isacsson U, Ekblad J (1998) Low Temperature Properties of Styrene-Butadiene-Styrene Polymer Modified Bitumens. Construction and Building Materials, 12: 405-414.

Lu X, Isacsson U (1997) Influence of Styrene-Butadiene-Styrene Polymer Modification on Bitumen Viscosity. Fuel 76(14/15): 1079-1180.

Muncy H W, King G N, Prudhomme B (1987) Improved Rheological Properties of Polymer-Modified Asphalts. ASTM Special Technical Publication, 941 (Asphalt Rheology): 147-165.

Nair N R, Mathew NM, Thomas S, Chatterjee P, Siddiqui MA (1998) Physical and Rheological Characteristics of Liquid Natural Rubber Modified Bitumen. J Appl Polym Sci 68: 53-61.

Polacco G, Vacin O J, Biondi D, Stastna J, Zanzotto L (2003) Dynamic Master Curve of Polymer Modified Asphalt from Three Different Geometries. Appl Rheol 13(3): 118-124.

Rassamdana H, Dabir B, Nematy M, Farhani M, Sahimi M (1996) Asphalt Flocculation and Deposition: I. The Onset of Precipitaiton. AIChE J 42(1): 10-22.

Rozeveld SJ, Shin EE, Bhurke A, France L, Drzal LT (1997) Network Morphology of Polymer Modified Asphalt Cements. Microscopy Research and Technique 38: 529-543.

Sabbagh A B, Lesser A J (1998) Effect of Particle Morphology on the Emulsion Stability and Mechanical Performance of Polyolefin Modified Asphalts. Poly Eng Sci 38(5): 707-715.

Singh B, Tarannum H, Gupta M (2003) Use of Isocyanate Production Waste in the Preparation of Improved Waterproofing Bitumen. J Appl Polym Sci 90: 1365-1377.

Singh B, Gupta M, Tarannum H (2003) Mastic of Polymer-Modified Bitumen and Poly(vinyl chloride) Wastes. J Appl Polym Sci 90: 1347-1356.

Stastna J, Zanzotto L, Vacin O J (2003) Viscosity Function in Polymer Modified Asphalt. J Colloid and Interface Sci 259(1): 200-207.

Varma R, Takeichi H, Hall JE, Ozawa YF, Kyu T (2002) Miscibility Studies on Blends of Kraton Block Copolymer and Asphalt. Polymer 43: 1-5.

Wen G, Zhang Y, Zhang YX (2002) Improved Properties of SBS-Modified Asphalt with Dynamic Vulcanization. Poly Eng Sci 42(5): 1070-1081.

Yousefi AA (2003) Polyethylene Dispersions in Bitumen: The effect of the Polymer Structural Parameters. J Appl Polym Sci 90: 3183-3190.

Zanzotto L, Stastna J, Ho K, (1996) Characterization of Regular and Modified Bitumens via Their Complex Modulus. . J Appl Polym Sci , 59: 1897-1905.

Zupancic A, Zumer M (2002) Rheological Examination of Temperature Dependence of Conventional and Polymer-Modified Road Bitumens. The Canadian J Chemical Eng 82(2): 253-263.

4.2. Rheological Investigation of the Influence of Acrylate Polymers on the Modification of Asphalt

4.2.1. Abstract

The effect of ethylene, ethylene acrylate and glycidyl methacrylate (EA) terpolymer, and ethylene butyl acrylate (EBA) copolymer on asphalt modification was investigated at 4, 6 and 8% polymer concentrations. Both melt state rheology and asphalt concrete mix (ACM) were investigated. In the melt state analysis, dynamic shear rheology, storage stability, artificial ageing and performance grading (PG) were studied. The PG grading of polymer modified asphalt (PMA) is correlated to the elastic properties of the polymers. Both resins enhanced the rheological properties; reduced the temperature susceptibility; showed better storage stability and extended the window of the PG of base asphalt. The two polymers showed similar ageing characteristics with little influence on flow activation energy. In asphalt concrete mix analysis, Marshall Stability, stripping, resilient modulus and permanent deformation tests were performed. Polymer modified asphalt concrete mix (PMACM) increased the percent retained stability and the resilient modulus of ACM. The elastic modulus of PMA and the resilient modulus of their ACM followed the same trend. Weak influence on water sensitivity was observed, but excellent rutting resistance was obtained for PMACM over ACM.

4.2.2. Introduction

Asphalt is widely used as an adhesive material in many fields (1), especially in pavement construction. A little amount of asphalt (4-6 percent by weight) is usually needed for acceptable pavement performance (2, 3). Asphalt concrete pavements,

however, suffers from different kinds of distresses like low temperature cracking, rutting, fatigue etc. (4-6). Moreover, increasing traffic volume, high traffic load and weather accelerate the pavement deterioration (2). So, asphalt binder should be stiff enough to resist rutting, flexible at low temperature to avoid thermal cracking and should have time independent properties as well as good fatigue and stripping resistances. Base asphalt is not capable of doing so; hence, modified asphalt is used. Among the different types of asphalt modification, polymer modification is done enormously (see Hussein et al., (7) and references therein).

In previous studies, asphalt was modified with selected polymers and the performance was evaluated for polymer modified asphalt (PMA) (7-16). In these studies, the effects of polymer type and content on compatibility, storage stability, rheology and ageing were investigated by rheological techniques. Polymer modification increased the complex shear modulus ($|G^*|$) of asphalt at intermediate and high temperatures and had little influence on $|G^*|$ and elastic modulus (G') at very low temperatures. Compatibility and storage stability were found to depend on polymer content, polymer type, and characteristics of base asphalt. Some researchers also introduced elementary sulfur in PMA and significant improvement in performance was observed (17-19).

The differential scanning calorimeter (DSC) was used to investigate the glass transition temperature of PMA (20, 21). The addition of small amount of polymer acts as a plasticizer and lowers the glass transition temperature of base asphalt. The effect of functional groups (acetate and acrylate) and grafted polymers on PMA and enhancement in rheological properties was examined (22). The polymer modification of asphalt is strongly manifested in the viscoelastic properties of PMA (13, 23). Performance of PMA

depends on ageing of asphalt, oil absorption by polymer particles and interaction of polymer particles with asphaltenes along with other factors (8, 12).

Usually, the improvement due to asphalt modification is evaluated by comparing the properties of asphalt concrete mix (ACM) to polymer modified asphalt concrete mix (PMACM) (24-29). Moreover, some researchers attempted to correlate the solid-state properties of base asphalt and PMA to that of ACM and PMACM, respectively (30, 31).

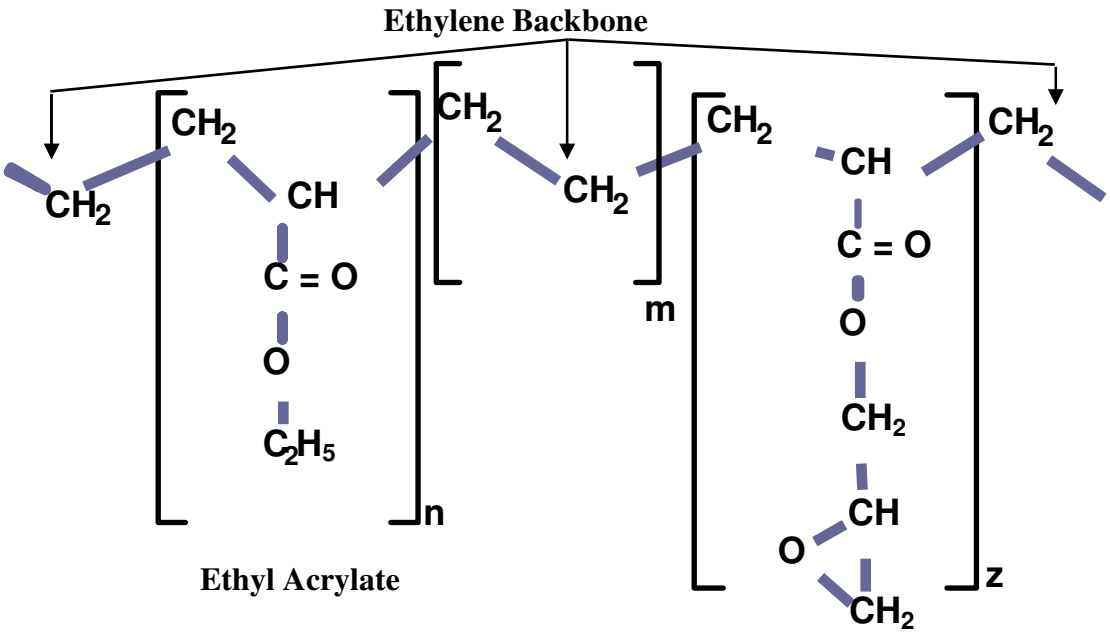
In this research, polymer modification of asphalt was carried out using two different acrylate polymers with different acrylate content and a comprehensive evaluation was performed to investigate the improvement in asphalt due to the modification. This evaluation contained two parts: study of the upgrade of asphalt performance due to polymer modification and its implication on the properties of ACM and PMACM. Most of the previous work has either focused on the rheology of PMA or the properties of ACM. In this study, we will try to examine the possibility of correlation between the properties of modified asphalt and their ACMs. Also, most of the previous work was carried out in cold climates (Canada & Sweden), where lower temperature properties of PMA were of great interest (4, 21, 22, 32). In this study, the high temperature performance is of interest for hot weather such as Arabian Gulf. In addition, most of the previous work has used polyethylene, ethylene vinyl acetate, or styrene butadiene styrene polymers. Data on asphalt modification with acrylate polymers were limited to studies on PMA (4, 22), regardless of its commercial use in some US roads, such as Oregon, Oklahoma, ..etc. Furthermore, the use of the previous polymers was limited to North American or European asphalts.

4.2.3. Experimental

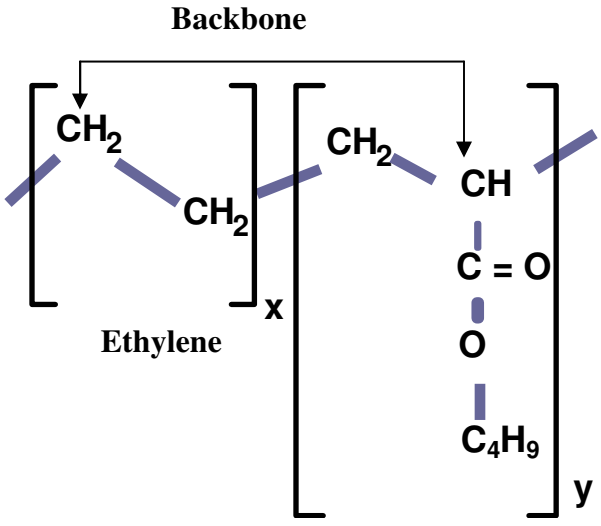
Materials

Two resins of acrylate polymers were used in this study. One was ethylene, ethyl acrylate and glycidyl methacrylate terpolymer (EA) containing more than 99% ethylene acrylate and the other was ethylene and butyl acrylate copolymer (EBA) containing 27% butyl acrylate (Figure 4.2.1). Both polymers were commercial polymers and they are marketed by DuPont as asphalt modifiers. Both polymers were used in USA with ELF asphalt (50/70 grade); however, they are yet to be tested with Arabian asphalt. Density, melting point, melt index (MI) at 190^{o}C/2.16 kg as provided by DuPont are given in Table 4.2.1. Number-average (M_n), weight-average (M_w) molecular weights and molecular weight distribution (MWD) were measured by a gel permeation chromatography (GPC) according and results are shown in Table 4.2.1. Details of the GPC characterization are given in a recent publication (7). The low density of EA is likely due to the high acrylate content. Asphalt, used in this study, was obtained from Saudi Aramco, Riyadh Refinery; and the results of the elemental analysis and asphaltene content of base asphalt were mentioned elsewhere (7). Asphalt used in this study contains about 30% asphaltenes as determined by the method of El-Mubarak.et al. (33).

Aggregates were collected form local sources. FTIR analysis of base asphalt showed very narrow peak at the wavelength of 3000 cm^{-1}, which indicates the presence of very small amount of –COOH group.



Ethylene Ethyl Acrylate and GMA Terpolymer (EA)



Ethylene and Butyl Acrylate Copolymer (EBA)

Figure 4.2.1: Molecular structure of EA terpolymer and EBA copolymer

Table 4.2.1: Characterization of Polymers

Polymer	**Density (g/cm^3)**	**Melting Point (^oC)**	**Melt Index (g/10min)**	**M_w (kg/mol)**	**MWD**
EA	0.576	52	8	91	5.61
EBA	0.926	94	4	80	4.23

Sample Preparation

Flat discs of as received polymer were prepared in a Carver Press for rheological tests. A mold temperature of ~20^{o}C above the melting point of each polymer was selected. Details of sample preparation in the Carver press are given elsewhere (7).

PMA samples were prepared by blending pre-weighed polymer with asphalt at 160^{o}C. The blending took place in a high shear blender (~2500 rpm) for a fixed time. The blending time was determined as 10 and 15 minutes for EA and EBA, respectively. This time was determined according to the procedure outlined in a previous publication (7). ACM and PMACM were prepared according to Marshall Mix design method (ASTM D 1559). Table 4.2.2 shows the details of mix design and values were obtained by following the standard test procedures. Standard cylindrical Marshall specimens (100 mm × 62.5 mm) were prepared for ACM and PMACM tests.

Rheological Characterization

Rheological tests of as received polymer, pure asphalt, and PMA were carried out in a strain controlled ARES rheometer. Nitrogen environment was used to avoid any possible degradation. Parallel plate geometry with a diameter of 25 mm and a gap of 1.5 mm was used in Advanced Rheometric Expansion System (ARES) rheometer. Strain amplitude of 20% was selected following separate strain sweep tests on asphalt, polymer, and PMA samples. This value was in the linear viscoelastic range.

Samples of 4% EBA-PMA from two different batches were tested for reproducibility to check for possible degradation (7) and results are plotted in Figure 4.2.2. Agreement of both viscous and elastic properties shows the excellent

reproducibility of these measurements. Dynamic frequency and temperature sweep tests were performed on all melts and test details were described elsewhere (7).

Storage Stability Test

This test helps in assessing the miscibility of polymer-asphalt blend, which is critical for storage and final use of PMA. The storage stability of the modified asphalt was evaluated according to Hussein et al. (7) $|G^*|$ values at 76^{o}C and 10 rad/s were measured in ARES rheometer for the top and the bottom samples and the difference was calculated. This temperature represents the required upper service temperature in the Gulf Countries (2). The test was carried out for PMAs containing 4% polymer.

Rolling Thin Film Oven (RTFO) Test

This test simulates the ageing process that takes place during the production and up to the first year of the service life of the pavement. The ASTM D 2872 procedure was followed to perform the RTFO test for PMA with 4% polymer. After completing the simulation, samples were collected for rheological testing in ARES. Moreover, Performance Grading (PG) of the 4% PMA was carried out according to the strategic highway research program (SHRP) specifications.

Marshall Stability Test

Marshall Stability was evaluated by measuring the compressive load required to break the ACM or PMACM specimen in a Marshall Testing Machine. The load was applied on the specimen at a constant deformation rate of 51 mm/min (2 in/min) and the load at failure was obtained. Six specimens were immersed into a water bath at 60^{o}C. After 40 minutes (initial condition), three specimens were tested and the average compressive load required to break the sample was determined. The remaining three

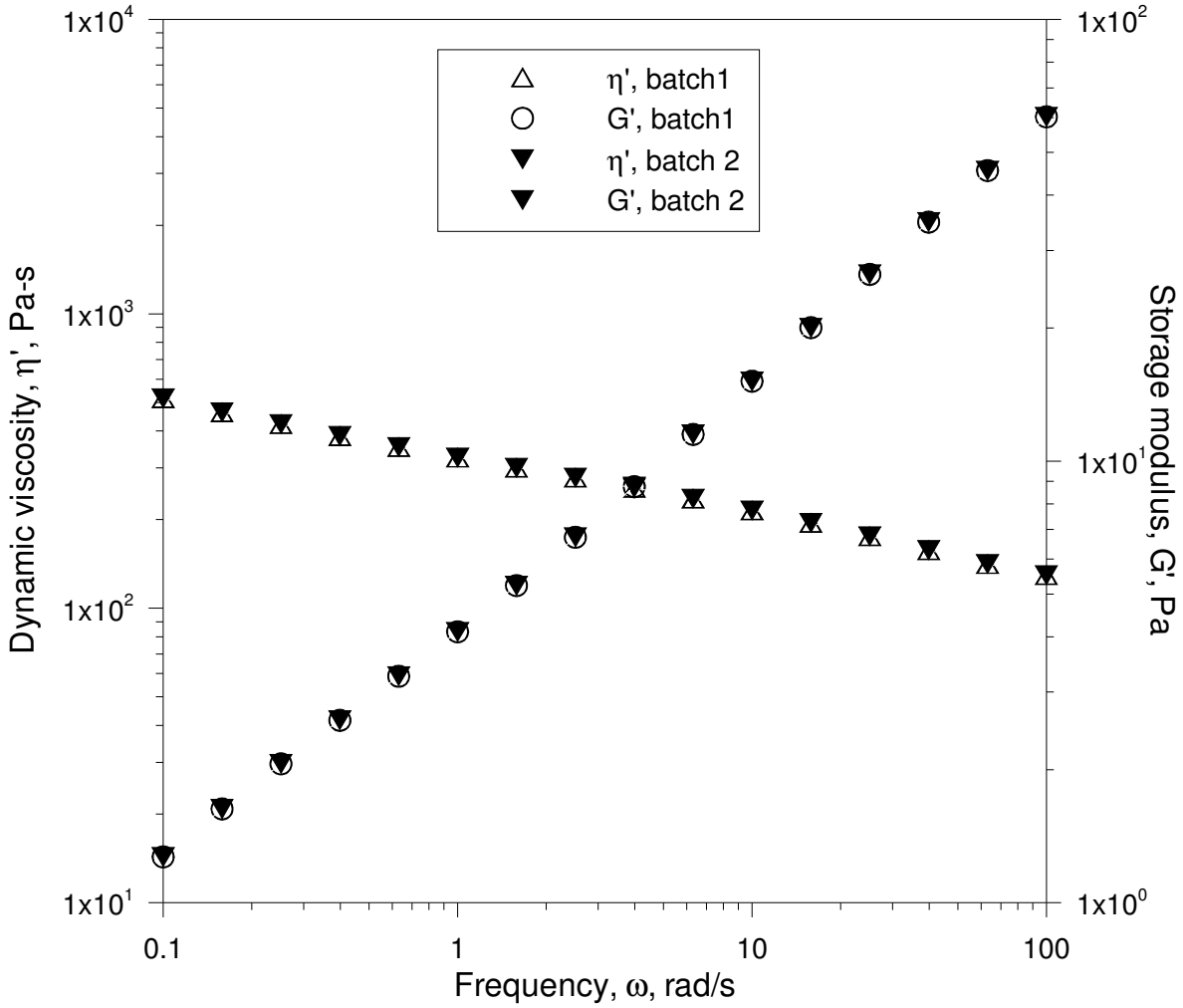


Figure 4.2.2: Batch reproducibility for the 4% EBA PMA (T_{blend} = 160°C, T_{test} = 76°C)

specimens were kept for 24 hrs (final condition) and the average compressive load was measured.

Stripping Test (Lottman Test)

This test shows the resistance of ACM and PMACM sample to water induced damage. It involves measuring the indirect tensile strength (ITS) at a constant deformation rate of 51 mm/min. ITS test was performed on compacted asphalt mixtures before and after saturation and accelerated water conditioning. Three specimens were immersed into water bath at room temperature for 2 hours and the average initial ITS was determined. For the measurement of the final average ITS, another three specimens were immersed in water under vacuum (20 in Hg) for 4 minutes to achieve 60% saturation, then samples were kept in a water bath at 60^{o}C for 24 hours, and finally immersed in another water bath at room temperature for 2 hours.

Resilient Modulus

Resilient modulus shows the pavement response in terms of dynamic stresses and corresponding strains. It is an important parameter for pavement design. A static load of about 10 lb was applied to hold the specimen in place and a repeated load in the linear range was applied at a frequency of 1 Hz. The resulting horizontal deformation was measured at 50^{o}C.

Permanent Deformation (Rutting) Test

Permanent deformation measurements were performed on ACM and PMACM at 50^{o}C. The controlled stress loading at 150 initial μ-strain level was used. The deformation was measured by linear variable differential transducer and data were stored in a data logger. The data were collected at every 5 seconds for the first 100 load repetitions; every

10 seconds for the next 100 repetitions; then every 15 seconds for the following 100 repetitions, and finally every 30 seconds up to the sample failure. Results were analyzed to compare the accumulated deformation due to repeated load in both ACM and PMACMs.

The rheological characterization, storage stability, and RTFO test were performed on asphalt and PMA. On the other hand, the Marshall Stability, water stripping (Lottman test), measurement of resilient modulus and rutting tests were carried out on asphalt concrete mixes.

4.2.4. Results and Discussion

Rheological Characterization

The results of dynamic frequency sweep tests on as-received polymer provided power law indices of 0.43 and 0.48 for EA and EBA, respectively. So, EA displayed higher shear thinning behavior than EBA, which explains the low blending time (10 min) determined from the separate measurement of G* as a function of time. Moreover, Table 4.2.1 shows that MFI of EA is higher than that of EBA; hence, less time was needed for blending of EA polymer. This observation supports the results of the dynamic shear rheology.

The dynamic viscosity, η', for EA-PMA are given in Figure 4.2.3 as a function of frequency, ω. Results are shown for the 4, 6 & 8% polymer content as well as base asphalt. Base asphalt showed typical Newtonian behavior over almost the entire ω range, but PMA displayed non-Newtonian behavior, which was more pronounced at high polymer concentrations. Similar behavior was observed for asphalt modification with other polymers (7, 35, 36). At low ω (ω = 0.1 rad/s), η' of the 4% EA modified asphalt is

~ 3 times higher than that of base asphalt; while at high ω (100 rad/s), η′ was ~2 times higher. Also, η′ increased at high polymer content; however, at high ω the effect of polymer concentration was not pronounced.

The shear thinning behavior of PMAs can be described by Carreau model:

$$\frac{G''}{\omega} = \eta' = \frac{\eta_o}{(1 + (\lambda_c \omega)^2)^s} \tag{4.2.1}$$

where, s is a parameter related to the slope of the shear-thinning region and λ_c is a characteristic time of the material. Excellent fit of Carreau model was observed for asphalt and PMAs as shown in Figure 4.2.3.

Data for η′(ω) of EBA PMA at three different polymer concentrations are presented in Figure 4.2.4. Addition of 4% of the polymer has increased η′ of PMAs at low-ω and resulted in a shear thinning behavior. The viscosity of the PMA in the range 100-0.1 rad/s is about 2-7 times that of base asphalt. For the same amount of polymer (4%), the enhancement of viscosity due to the addition of EBA is almost twice that of EA. It should be noted that the EA terpolymer had an MFI that is twice that of EBA copolymer (see Table 4.2.1).

High values of G′ suggest low resistance to low-temperature cracking. Hence, EA is expected to have better low-temperature cracking resistance than EBA as confirmed later by PG tests in the bending beam rheometer. Figures 4.2.5 and 4.2.6 show data for G′(ω) of EA and EBA modified asphalt, respectively, at three different polymer concentrations. Polymer modification increased G′ value of base asphalt. The value of G′ for the 4% EA PMA was more than four times that of base asphalt and it increased at higher polymer contents. The influence of polymer content was not that much strong for EA since the test temperature (76^{o}C) is above the melting point of EA (52^{o}C). Therefore,

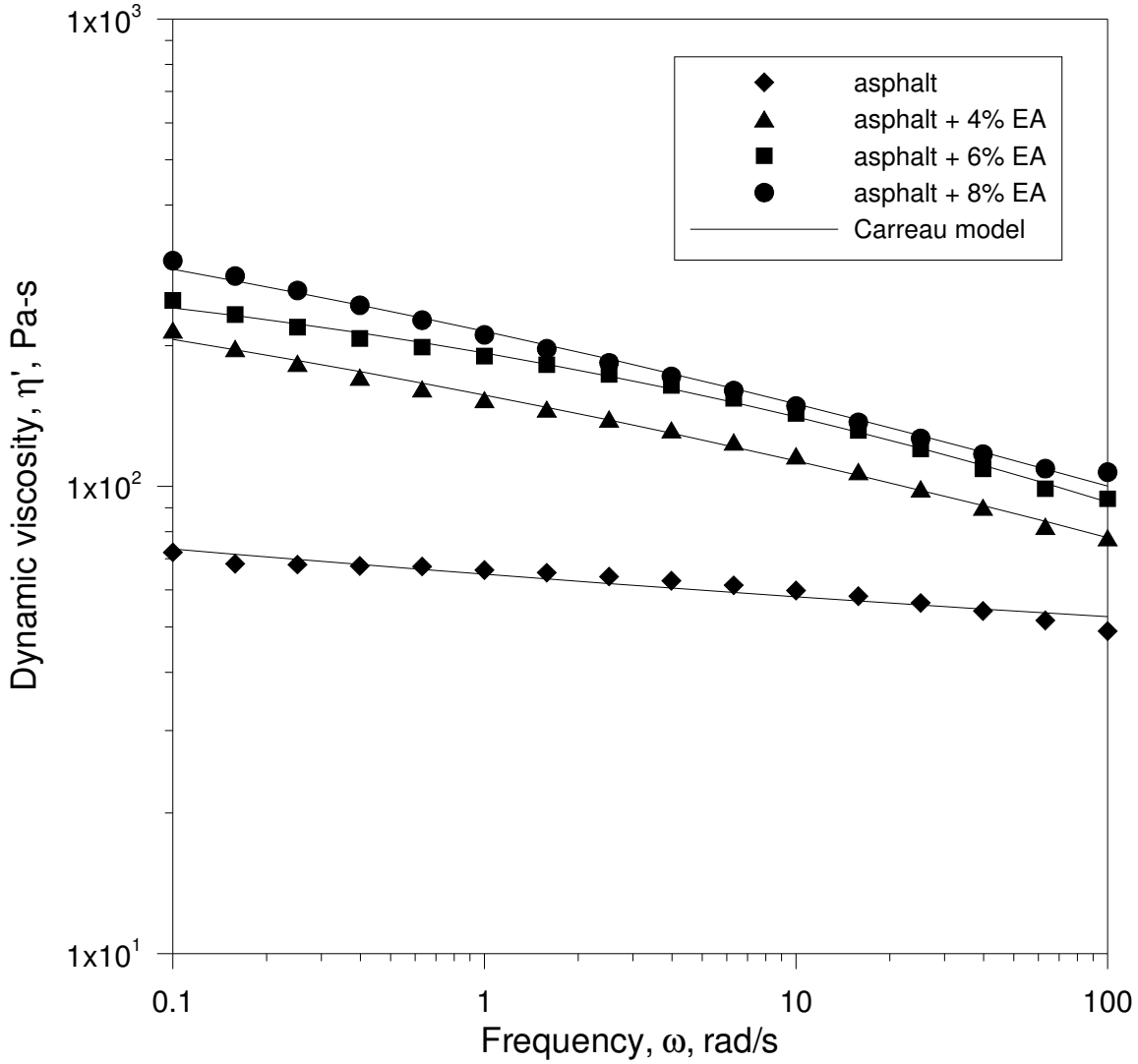


Figure 4.2.3: η′ (ω) for EA modified asphalt at different EA concentrations (T_{test} =76^{o} C).

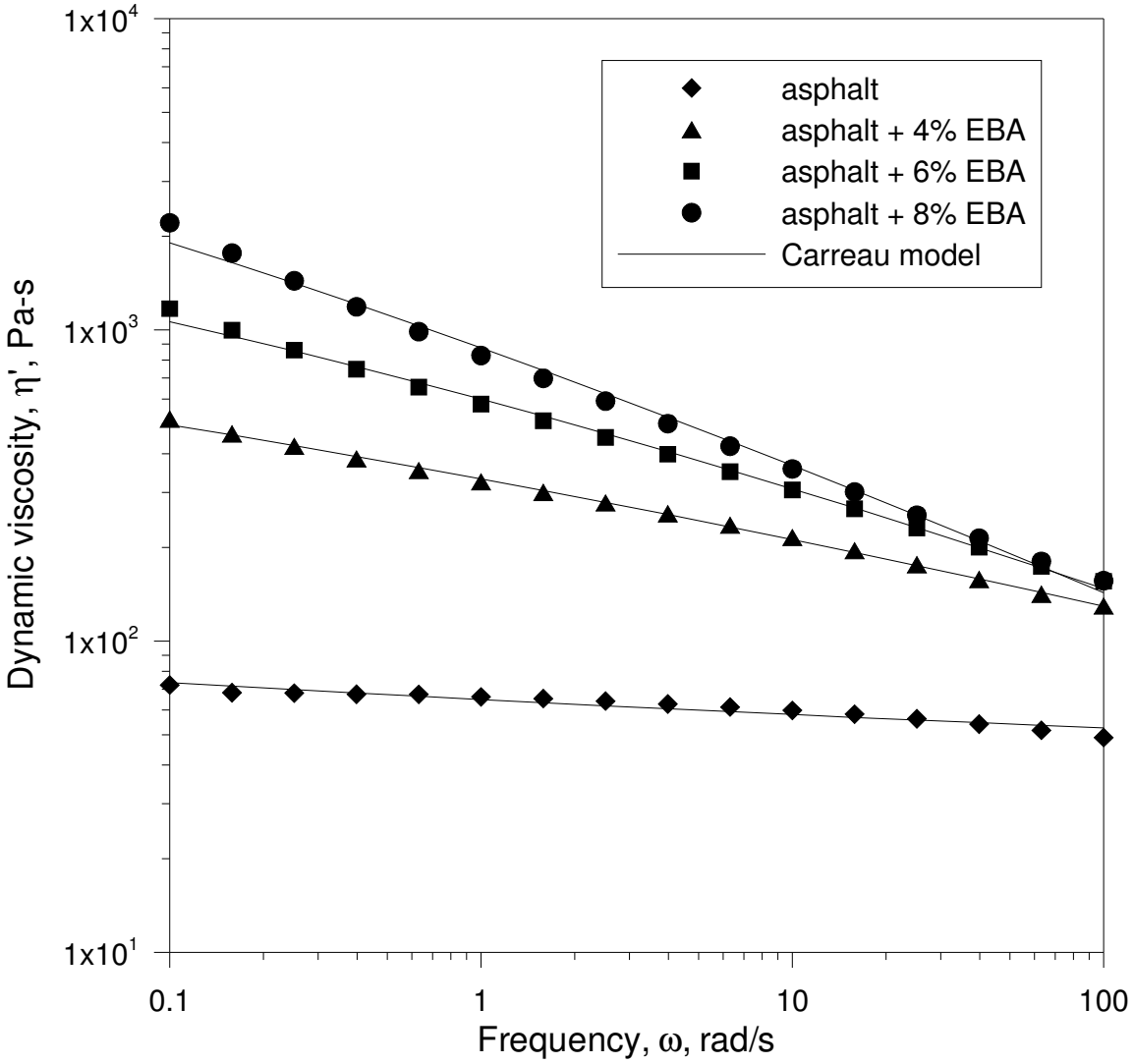


Figure 4.2.4: η′ (ω) for EBA modified asphalt at different EA concentrations (T_{test}=76^{o}C)

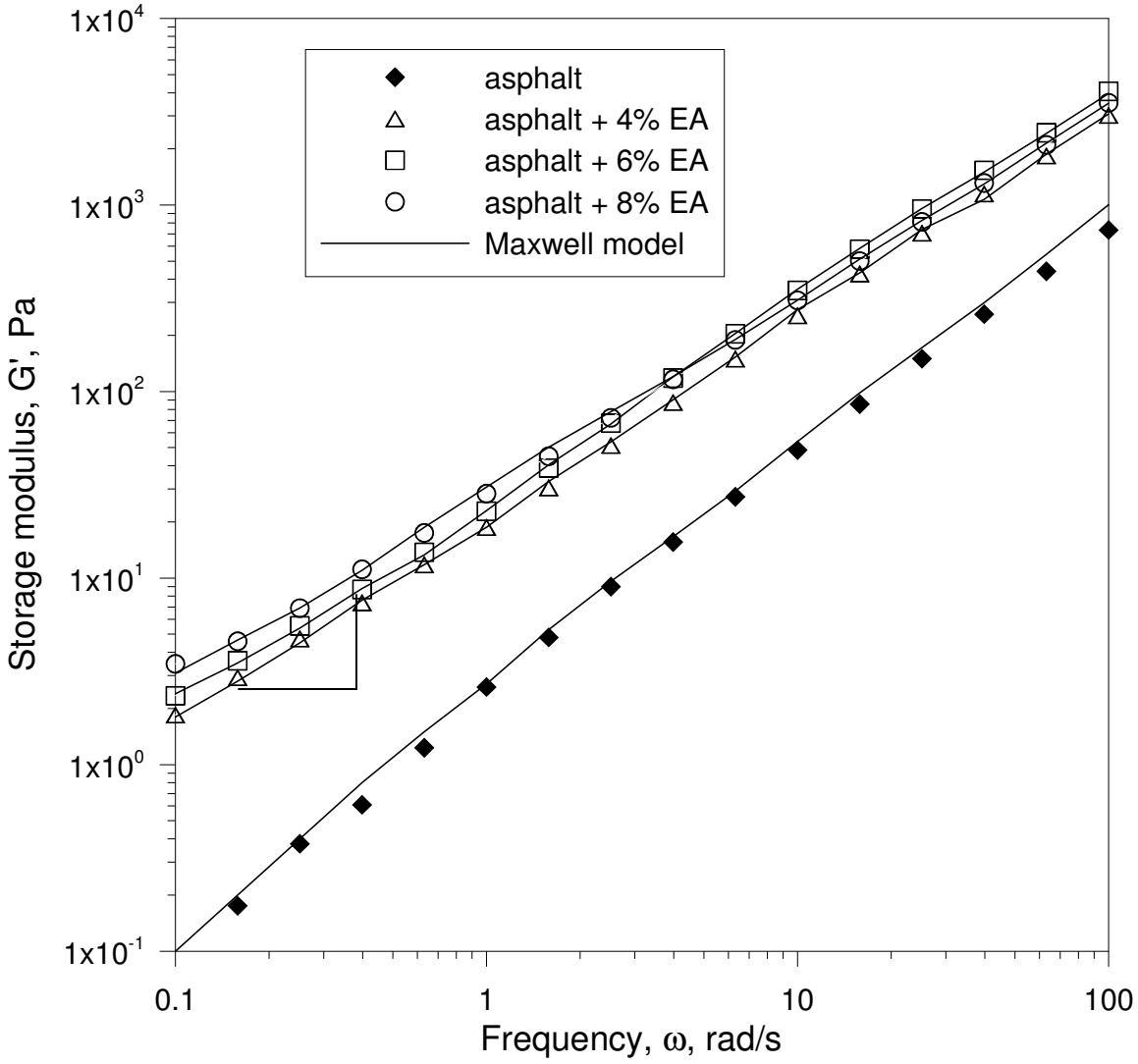


Figure 4.2.5: G′ (ω) for EA modified asphalt at different EA concentrations (T_{test}=76°C).

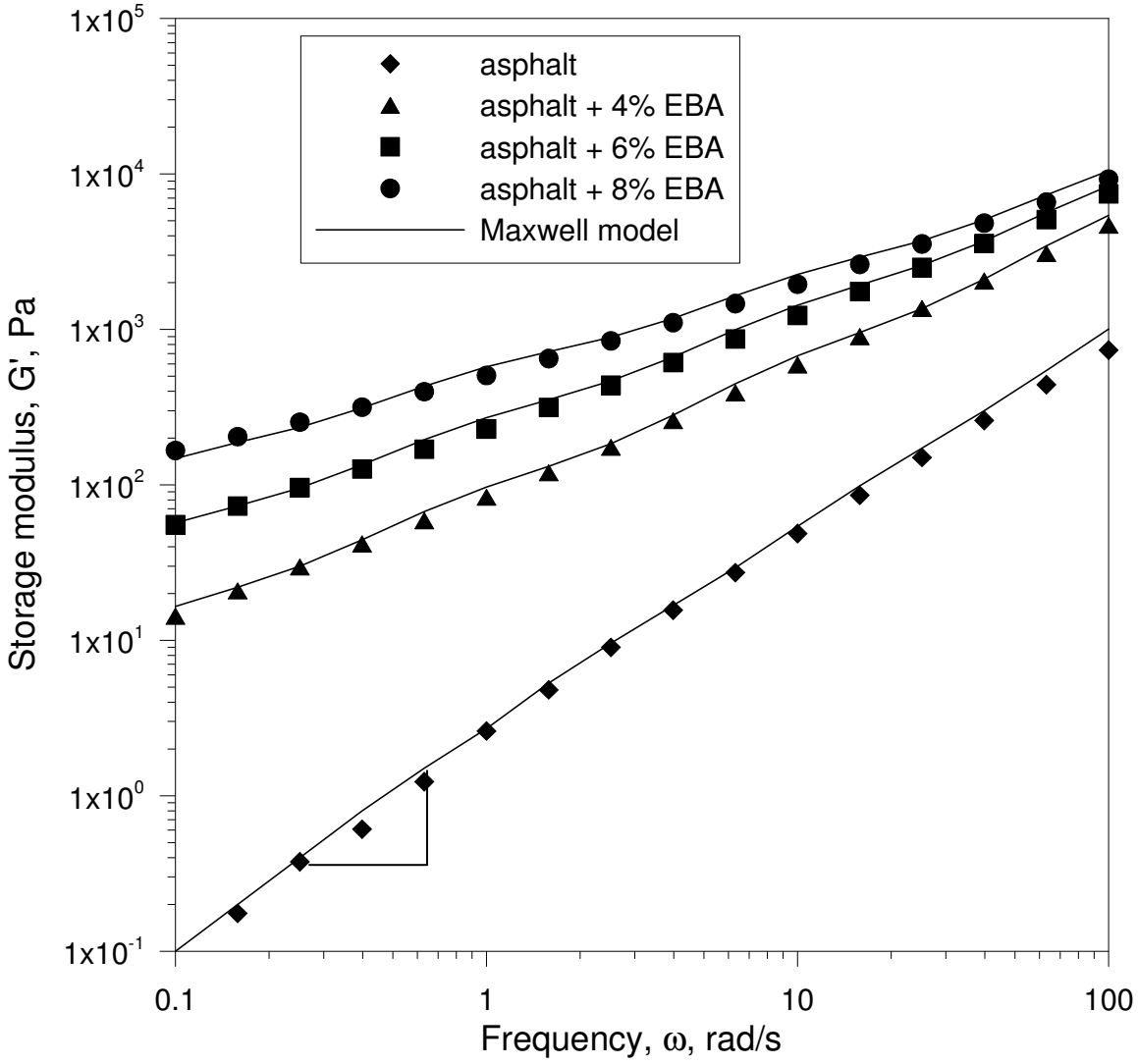


Figure 4.2.6: G′ (ω) for EBA modified asphalt at different EBA concentrations (T_{test}=76°C).

a weak influence of polymer concentration on G′ is evident. For EBA, the increase in G′ with the increase of polymer concentration is attributed to its high melting point (94^{o}C).

Similar improvements were observed in previous research (1, 9, 10). So, EBA shows higher G′ at low ω, which suggest better flexibility. According to the principle of time-temperature superposition, this behavior corresponds to long service time or high G′ at higher temperature, which is needed in hot climate. The slopes of log G′ vs. log ω at low ω were 1.43, 1.04, 0.81 and 0.6 for base asphalt, the 4, the 6 and the 8 wt% EA PMA (see Figure 4.2.5), respectively. However, for the 4, the 6 and the 8% EBA modified asphalt the slopes are 0.76, 0.61 and 0.48, respectively (see Figure 4.2.6). It can be observed that for the same polymer content, the slope for EBA-PMA was less than that of EA-PMA. So, EBA shows higher G′ at low ω. So, the melt rheology of EBA-PMA suggests that EBA is expected to show better deformation resistance at high temperature.

Analysis of viscoelastic data was extended to mechanical spectra to obtain a detailed overview of rheological properties due to polymer modification of asphalt. G′(ω) was described by the generalized Maxwell model. In the linear viscoelastic range, the model leads to the following expressions for G′ as a function of ω:

$$G' = \sum_i \frac{H_i \lambda^2{}_i \omega^2}{(1 + \lambda^2{}_i \omega^2)} \qquad (4.2.2)$$

where λ_i and H_i are relaxation time and elastic modulus of i^{th} Maxwell element. Here, 7 sets of Maxwell elements were considered to avoid any problems concerning the evaluation of fitting parameters λ_i and H_i. Under these conditions, the model was able to describe the mechanical spectra of all asphalt and PMAs in Figures 4.2.5 and 4.2.6.

Figure 4.2.7 shows the relaxation spectra, [H(λ)], of asphalt and PMAs at 76^{o}C. In this case, 15 set of Maxwell elements were considered to get good fit. It can be observed

that H for base asphalt has rapidly decreased with the increase of λ. It means, decrease in elastic properties for asphalt is high with time. This decrease is less for PMAs and the 8% EBA PMA showed the least decrease. EBA copolymer has shown a slower rate of decrease in H with λ and H(λ) for EBA is always higher than that of EA. This suggests that EBA modified asphalt has maintained higher values of elastic properties and looses its elasticity at a slower rate in comparison with EA-PMA. These results are consistent with our previous data for G′ of EBA-PMA shown in Figure 4.2.6.

Figure 4.2.8 shows the results of η*(T) for EA terpolymer obtained from temperature ramp tests. η* was found to increase significantly for the 4% EA PMA and this increase was higher for high EA content. At high temperature, high values of G* (G*= η*ω) are needed. High η* indicates the high rutting resistance at high temperature. No significant difference in η* was observed between the 6% and the 8% EA modified asphalt 50^{o}C. But at higher temperatures (~70^{o}C) the influence of polymer content on η* is noticeable.

Viscosity-temperature relationships of PMAs can be expressed by the well known Arrhenius equation.

$$\frac{G^*}{\omega} = \eta^* = Ae^{E_a/RT} \qquad (4.2.3)$$

where E_a is the flow activation energy, A is the pre exponential term and R is the universal gas constant. E_a is an important factor that strongly influences the viscosity. The data given in Figure 4.2.8 showed excellent fit to Arrhenius equation.

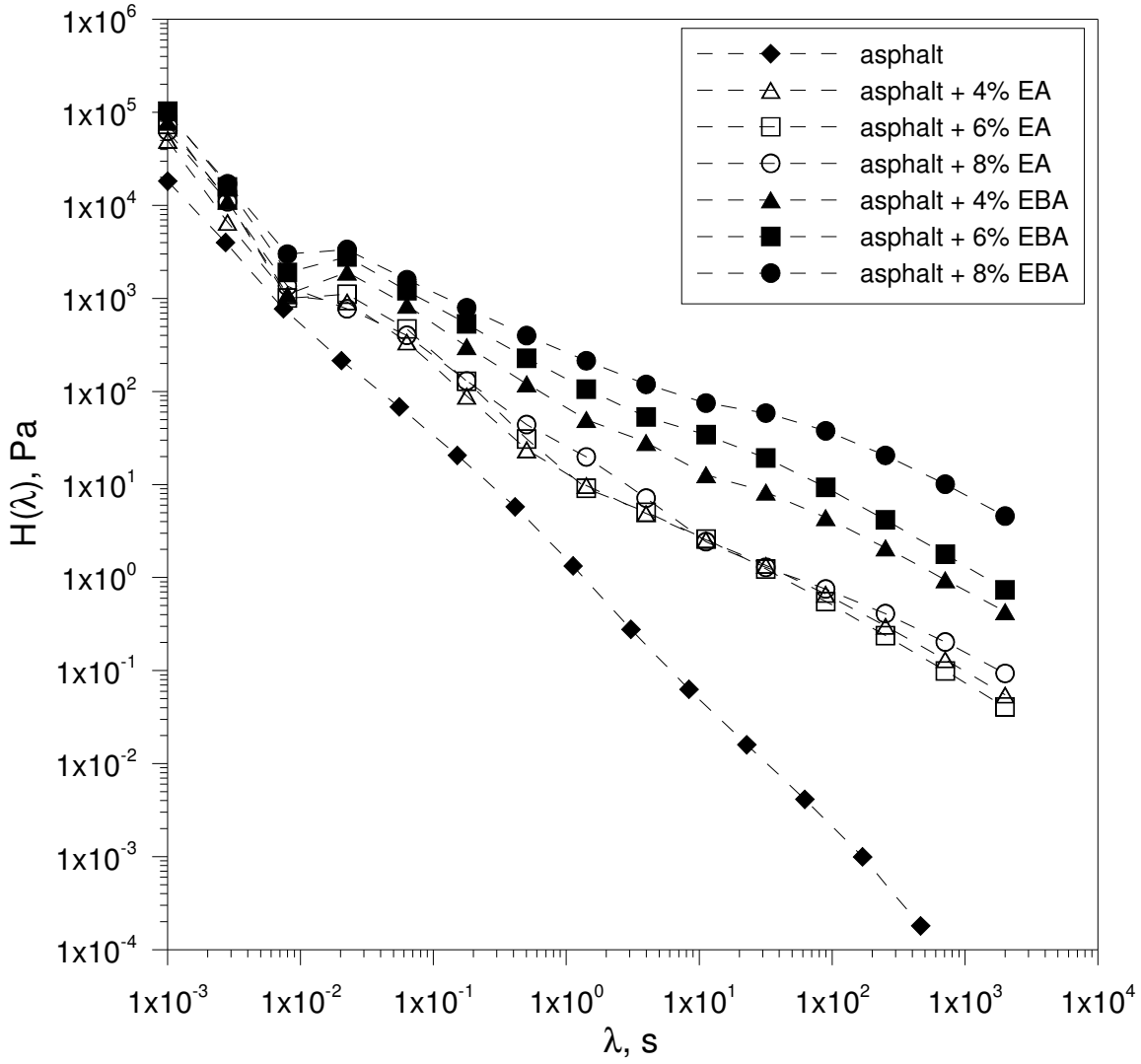


Figure 4.2.7: Relaxation spectrum of asphalt and PMAs (T_{test} =76°C).

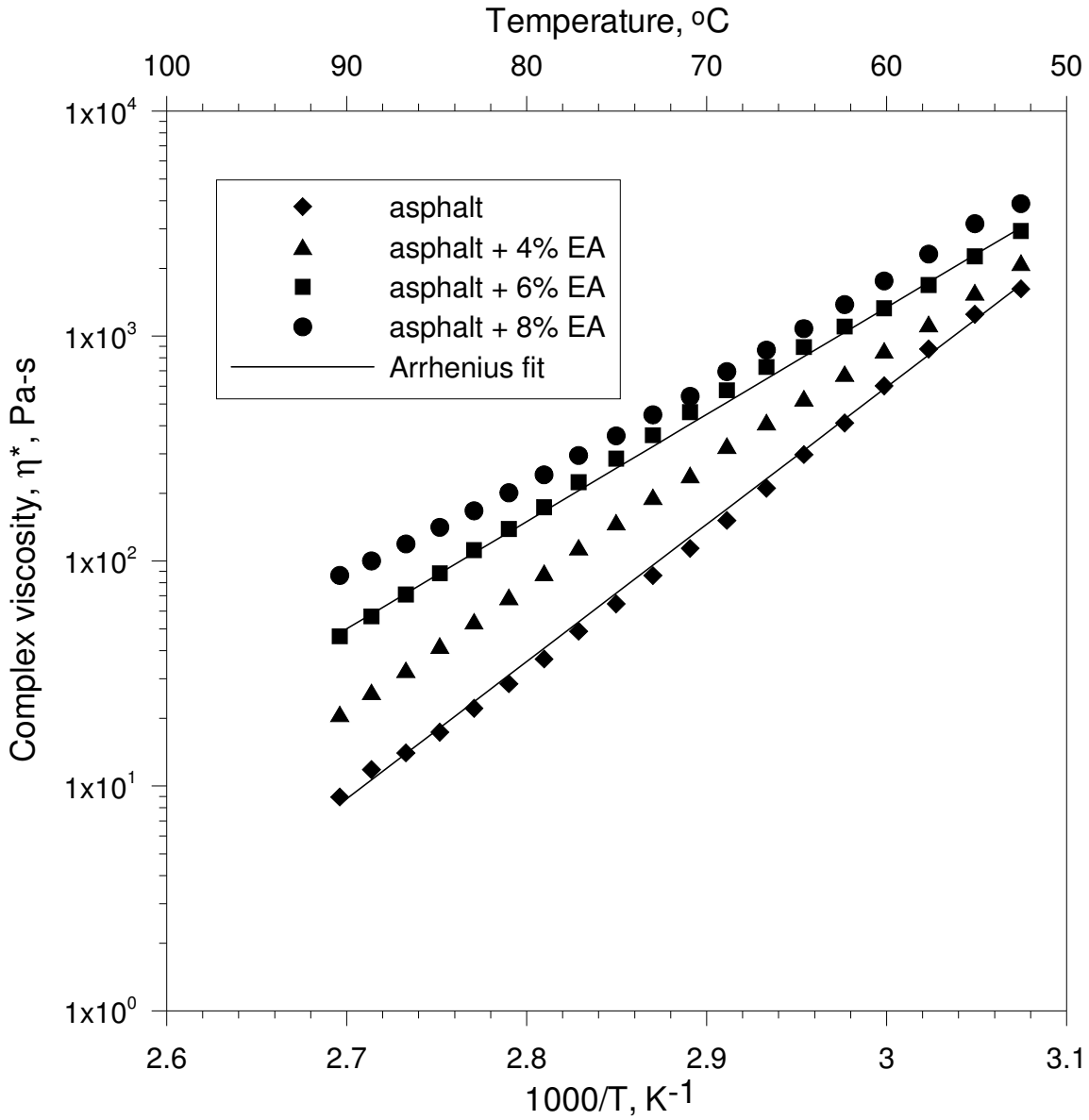


Figure 4.2.8: η*(T) for EA modified asphalt at different EA concentrations (ω = 10 rad/s)

To prevent high temperature rutting, asphalt should be more elastic at elevated temperature. One of the objectives of polymer modification is the lowering of E_a in comparison to base asphalt. So, viscosity changes with temperature should be low and relatively high η* (or G*) is desirable at high temperature. Temperature ramp tests data were also used to obtain E_a and A from equation (3). Figure 4.2.9 shows the plot of E_a vs. polymer concentration. A good linear relation between E_a and weight fraction of polymer was obtained for both polymers and the relations are displayed on the plot. The 8% EA reduced E_a of base asphalt from 114 kJ/mol to as low as 82.96 kJ/mol. On the other hand, the addition of 8% EBA reduced E_a to 99.4 kJ/mol. So, for the 4% polymer concentration, the influence of EA and EBA on activation energy is comparable.

According to SHRP, PMA should have a minimum $|G^*|/\sin\delta$ of 1 kPa at its upper service temperature. Base asphalt showed a $|G^*|/\sin\delta$ of 1 kPa at 70.96°C. However, the 4% EA and the 4% EBA PMA showed the same value at 79.48°C and 85.46°C, respectively. So, further analysis was performed on the 4 wt% polymer samples since both PMAs satisfy the SHRP specifications at this concentration.

Storage Stability

Addition of polymer enhances the complexity of asphalt since asphalt contains different phases (23, 37, 38). Practically, asphalt is stored at elevated temperature, which accelerates the phase separation of PMA into asphalt and polymer rich phases. Initially, the blend was homogeneous and there was no difference in $|G^*|$ value between the top and the bottom of the container. After 72 hrs of continuous mixing at 160°C in the presence of air, all polymers showed $|G^*|$ values that are high both at the top and at the

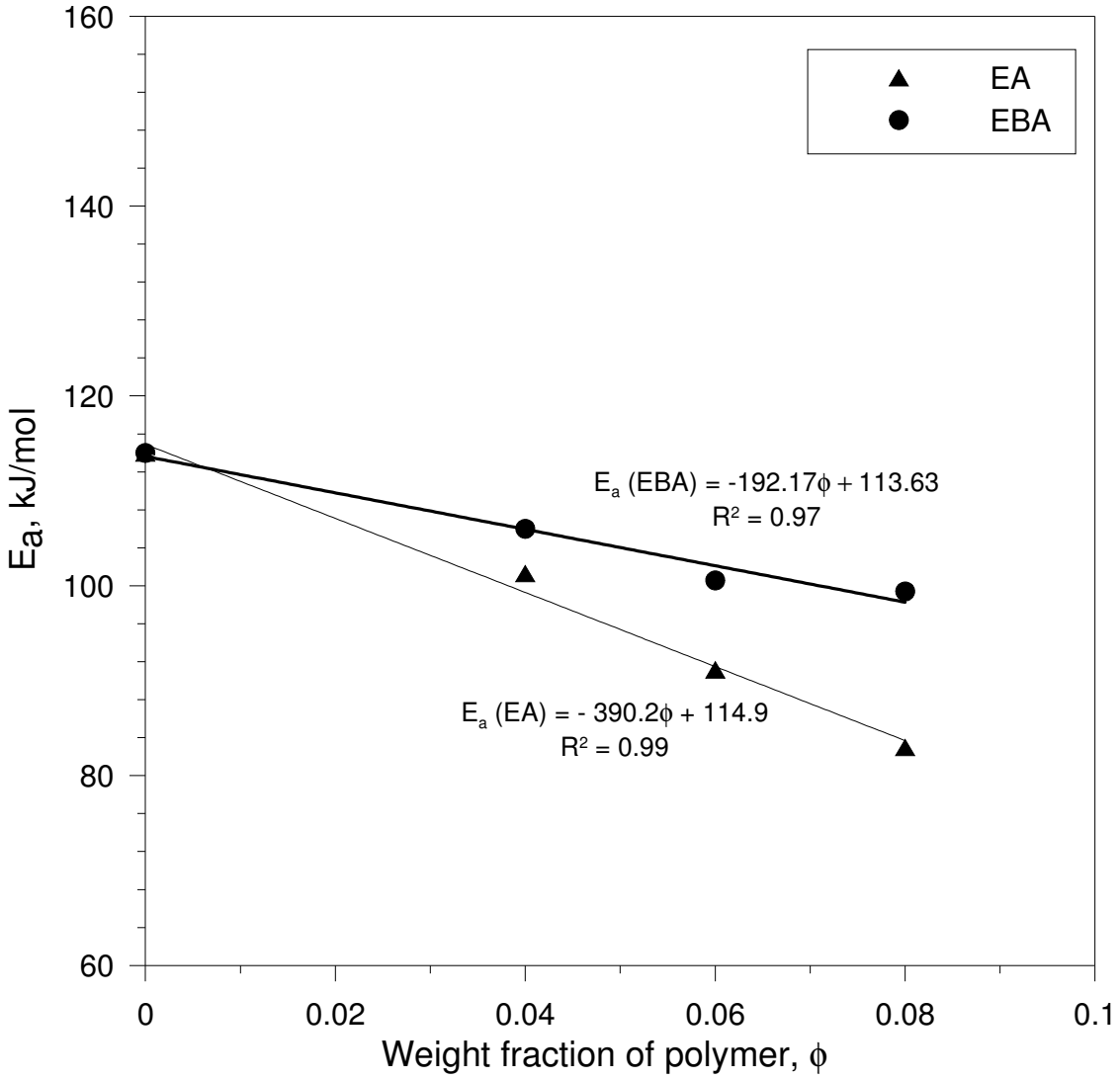


Figure 4.2.9: Plot of E_a vs. weight fraction of polymer

bottom. Moreover, there was a difference in $|G^*|$ value between the top and the bottom. The percent differences were 8.81 and 16.06% for EA-PMA and EBA-PMA, respectively. The high temperature and long mixing time would result in considerable oxidation that would eventually lead to the observed increase in $|G^*|$. So, phase separation in EBA-PMA was higher than that of EA-PMA. However, both PMAs showed good storage stability that is within the acceptable limit of 20% (39).

Also, relaxation spectra were used in Figure 4.2.10 ($\lambda^*H(\lambda)$ vs. λ) to observe the immiscibility of asphalt polymer blend. In this kind of plots, a single phase pure component shows a single peak, which reflects the complete homogeneity, but multi phase systems show more than one peak. In this case, the 4% of EA and EBA PMA were compared with base asphalt. At low λ (~0.001 s), base asphalt showed a broad peak a characteristic of the multiphase nature of asphalt constituents. Both PMAs showed similar behavior at low λ. The low λ peak (λ~0.01 s) is likely due to the low Mw asphalt phase, while higher peaks represent the polymer phase. For EBA, the second peak was observed to be broader than that of EA. This implies that EBA PMA has great tendency for phase separation in comparison to EA-PMA. Similar behavior was observed in storage stability, where the percentage difference in $|G^*|$ value between the top and the bottom samples was higher for EBA-PMA.

The supplier of the polymer resins claimed that no percent difference was observed between the top and the bottom for the polymers in the storage stability test. The reason could be the –COOH content. Asphalt, used in this study, contains small amount of –COOH group. So, insufficient reaction between –COOH and the polymers were occurred to form homogeneous phase.

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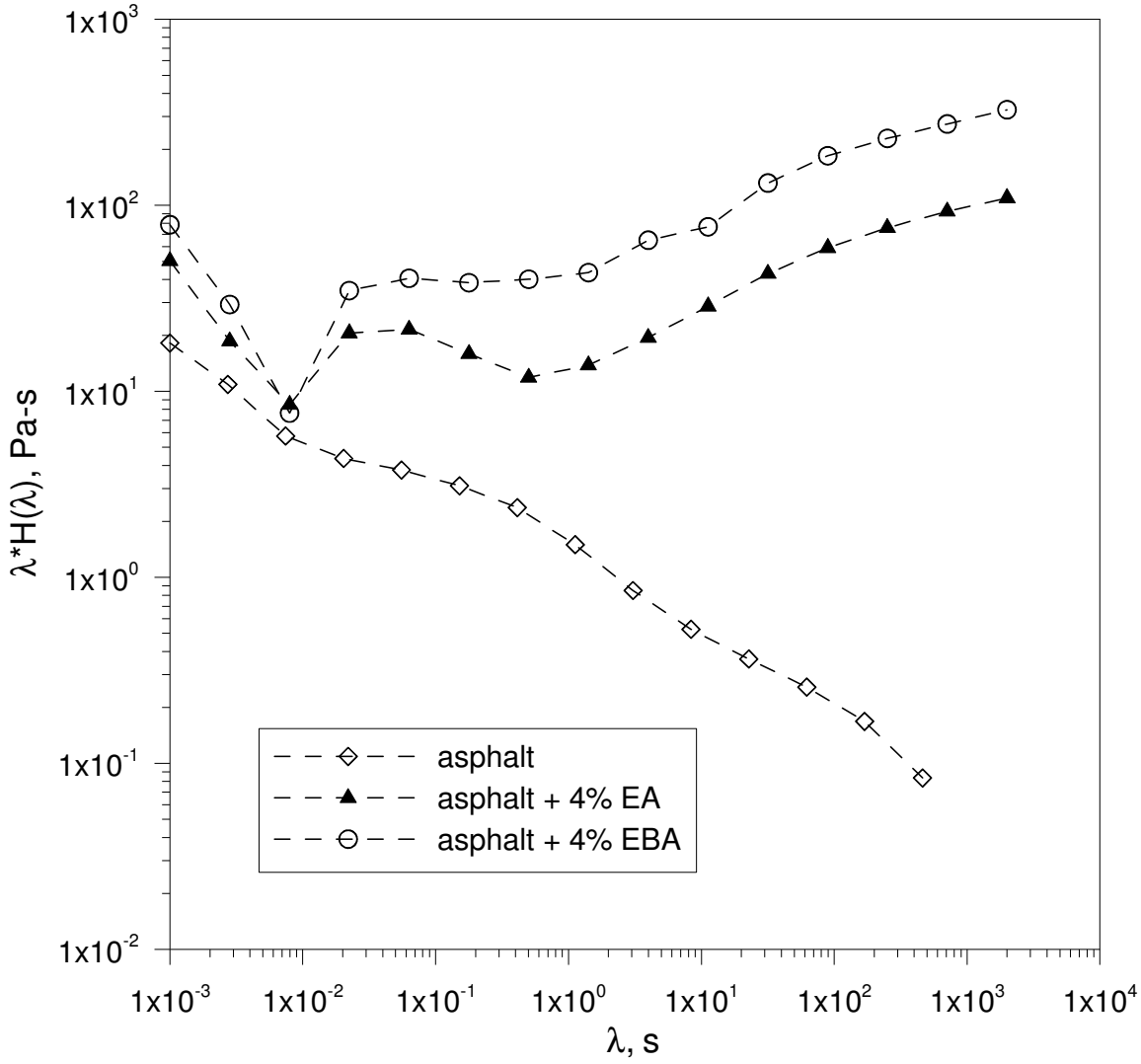

Figure 4.2.10: Plot of λ*H(λ) vs. λ for asphalt and 4% of EA and EBA PMA (T_{test}=76°C).

Rolling Thin Film Oven (RTFO) Test

Figure 4.2.11 shows the effect of short term ageing on base asphalt and PMAs. It is clear that ageing increases η* with little or no influence on flow activation energy (the lines are almost parallel). The viscoelastic properties of aged specimens are generally higher than those of unaged ones. High ageing temperature (160^{o}C) favors the volatilization of low M_w constituents of asphalt and degradation of the polymer. High M_w constituents remain in the asphalt. Polymer degradation can lead to either x-linking or chain scission depending on the chemistry of the polymer degradation (34). The rheological changes of aged asphalt depend on the combined effect of asphalt oxidation and polymer degradation. The polymer degradation is influenced by polymer type and concentration, molecular structure, residual catalyst … etc. In this case, x-linking is favored, which is likely due to the formation of free radicals as a result of the combined effect of heat and shear.

Performance Grading (PG) of PMA

The PG of local PMA should have a PG of 76-10 (2). The 76^{o}C refers to the upper service temperature, while the -10^{o}C is the lower temperature. The PG for base asphalt is 64-22. For the 4% EA-PMA and the 4% EBA-PMA, the PG was 76-16 and 82-10, respectively. So, modified asphalt showed higher service temperature in comparison with base asphalt. EBA polymer showed higher upper service temperature than that of EA polymer (82 ^{o}C vs. 76 ^{o}C). On the other hand, EA modified asphalt displayed lower service temperature than that of EBA. The more viscous EBA has shifted the service

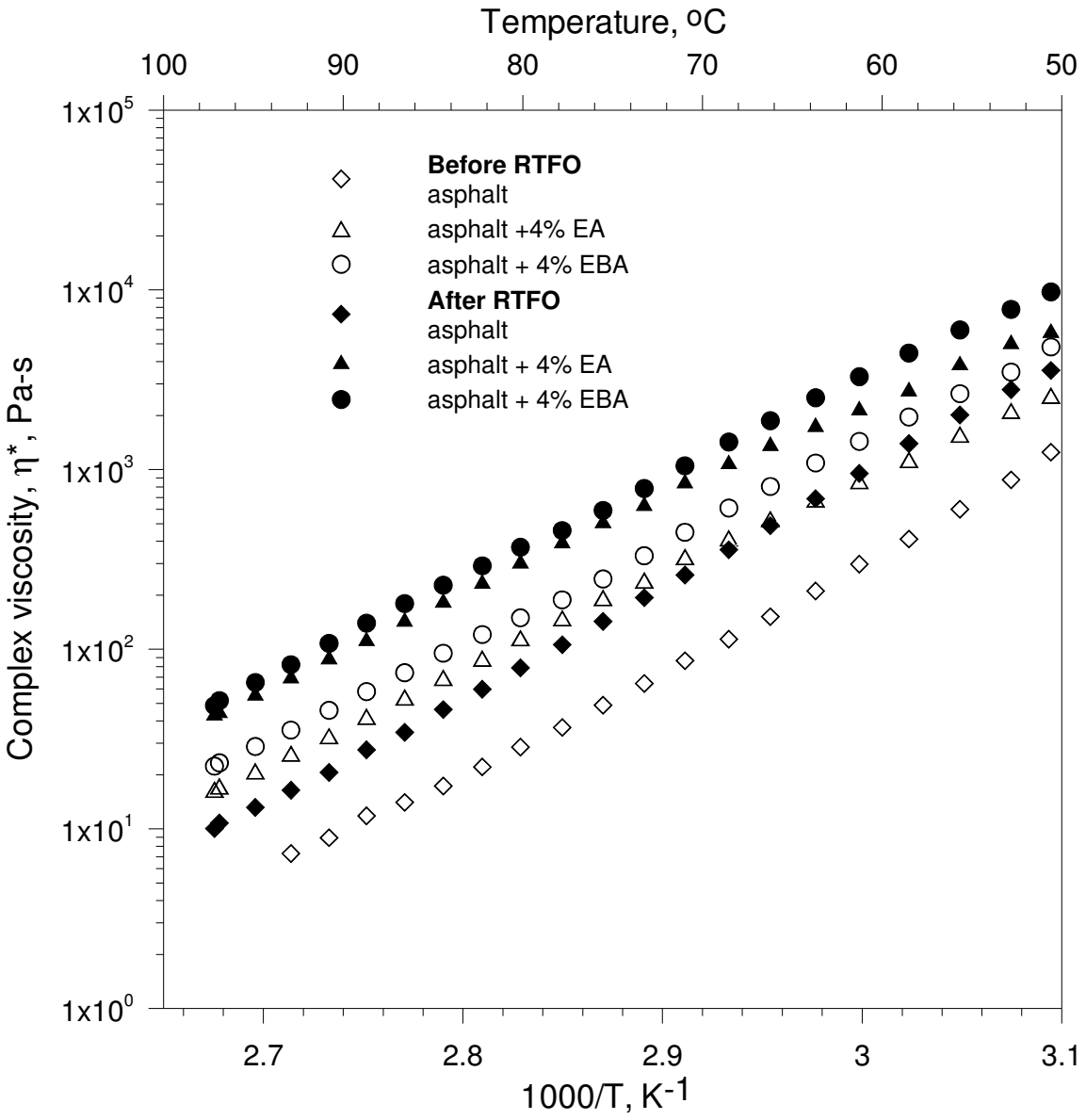

Figure 4.2.11: Effect of ageing on η*(T) (ω = 10 rad/s).

temperature window to the right. So, the PG grading of PMA is correlated to their elastic properties.

Polymer modification improved the performance of base asphalt at every melt state analysis described so far. EBA polymer increased the value of rheological properties like G′(ω), η′(ω) and η*(T) compared to EA. But the influence on E_a was comparable. Moreover, better storage stability was observed for EA polymer. In general, addition of 4% of EA or EBA resulted in acceptable performance. However, EBA showed better PG and G′ that are important for high temperature performance.

Marshall Stability Test

The required compressive loads to break ACM and PMACMs are presented in Table 4.2.3. Three specimens for each condition (initial and final) were used and the average compressive load, with standard deviation, is reported in Table 4.2.3. The load required to break PMACMs was less than that of ACM. The percent loss in compressive load due to conditioning at high temperature is reported in Table 4.2.3. This loss was the highest for ACM and the least for EA PMACM. The percent loss for EBA PMACM was in the acceptable 20% limit (36). So, the percent retained stability for PMACMs was higher than that of ACM and EA modified asphalt had better Marshall stability. For the 4% PMA, the results given in Figures 3-6 indicate that EBA-PMA had higher viscous and elastic properties than EA-PMA, followed by base asphalt. However, the results of the Marshall stability do not correlate with the melt rheology of their PMA.

Table 4.2.2: Mix design method

	Job Mix Formula (JMF)	**Specification Limits**
1. Optimum Asphalt Content, % (60/70 Pen grade asphalt)	5.3	5.3 +/- 0.3
2. Marshall Test Results (75 blows, compaction temperature 150^{o}C)		
Stability (Kg)	1804	800 Min.
% Air Voids. Total Mix	4.4	4.0 - 6.0
Flow (mm)	3.2	2.0 - 4.0
% Voids filled w/asphalt	74	70 - 80
Stability Loss, (%)	16.2	20 Max.
Void in Mineral Aggregates (VMA)	16.04	-

Stripping Test (Lottman Test)

The average indirect tensile strength (ITS) for ACM and PMACMs is shown in Table 4.2.3. Three specimens of each sample were used and the standard deviation is reported for the initial and final conditions along with percent loss due to accelerated water damage. The percent loss in ITS was obtained for EBA- and EA-PMACMs, and compared to ACM. Values of the percent loss are in the range of 31-36%. Accelerated saturation by using vacuum and long time exposure in high temperature water bath weakened the bond between PMACM and aggregates. This is the reason for the loss in ITS due to conditioning. It is quite clear that the water sensitivity properties of asphalt and PMAs are similar. So, polymer modification had no influence on the stripping properties of ACM. The water stripping in ACM is more of a chemical rather than a physical property. So, we did not attempt to correlate it with rheological properties of PMA.

Resilient Modulus (M_R)

Resilient Modulus obtained at 50^{o}C for ACM, EA PMACM and EBA PMACM are 66.15, 90.79 and 116.73 ksi, respectively. So, polymer modification increased M_R of base asphalt by 37.2% and 76.46% for EA and EBA, respectively. Similar behavior was obtained for PMACM in the previous studies (40, 41). Here, we attempted to check for a possible relationship between the resilient modulus of ACM and the elastic modulus of PMA. Qualitatively, the trend of the increase in G′ in asphalt, EA-PMA, and EBA-PMA was the same as that of their corresponding ACMs. So, there exists a qualitative relationship between G′ of PMA and M_R of PMACM.

Permanent Deformation (Rutting) Test

Figure 4.2.12 shows the results of accumulated strain vs. the number of repeated loads. Polymer modification decreased the deformation of concrete mix i.e. increased the rutting resistance. Similar observations were reported for modification with other polymers (25, 42). Lower deformation of PMACM indicates the elastic nature of PMA, which is attributed to polymer modification. The slopes and anti-logs of intercepts were obtained in the linear region. The slopes were 0.6, 0.2 and 0.2 for ACM, EA and EBA PMACMs, respectively. Anti-logs of the intercepts were 0.0045, 0.0205, and 0.0316 for ACM, EA and EBA PMACMs, respectively. PMACM showed less accumulated strain in comparison with ACM, which suggests improvement in rutting resistance due to the addition of polymers. Although the slope of both PMACMs is the same, but the anti-log of intercept is smaller for EA-PMACM, which suggests higher rutting resistance. Therefore, the more elastic EBA-PMA showed the lower rutting resistance than EA-PMA. So, there is no correlation between the melt rheology and the permanent deformation properties of the ACM.

At the high number of repetitions, the deformation was gradual for ACM, while PMACMs showed rapid deformation. Both polymers contain rigid carbonyl group, which bears double bond and makes the polymer highly elastic and tough. After a certain critical number of repeated load, PMACM breaks. The critical number of repeated loads is 70,000 and 110,000 for EBA and EA-PMACM, respectively. The number of repeated loads required for complete failure of the concrete mix was 4255, 121487 and 71273 for ACM, EA and EBA PMACMs, respectively. These values indicate the high rutting resistance behavior of EA-PMACM. Also, similar endurance limit for EA was reported

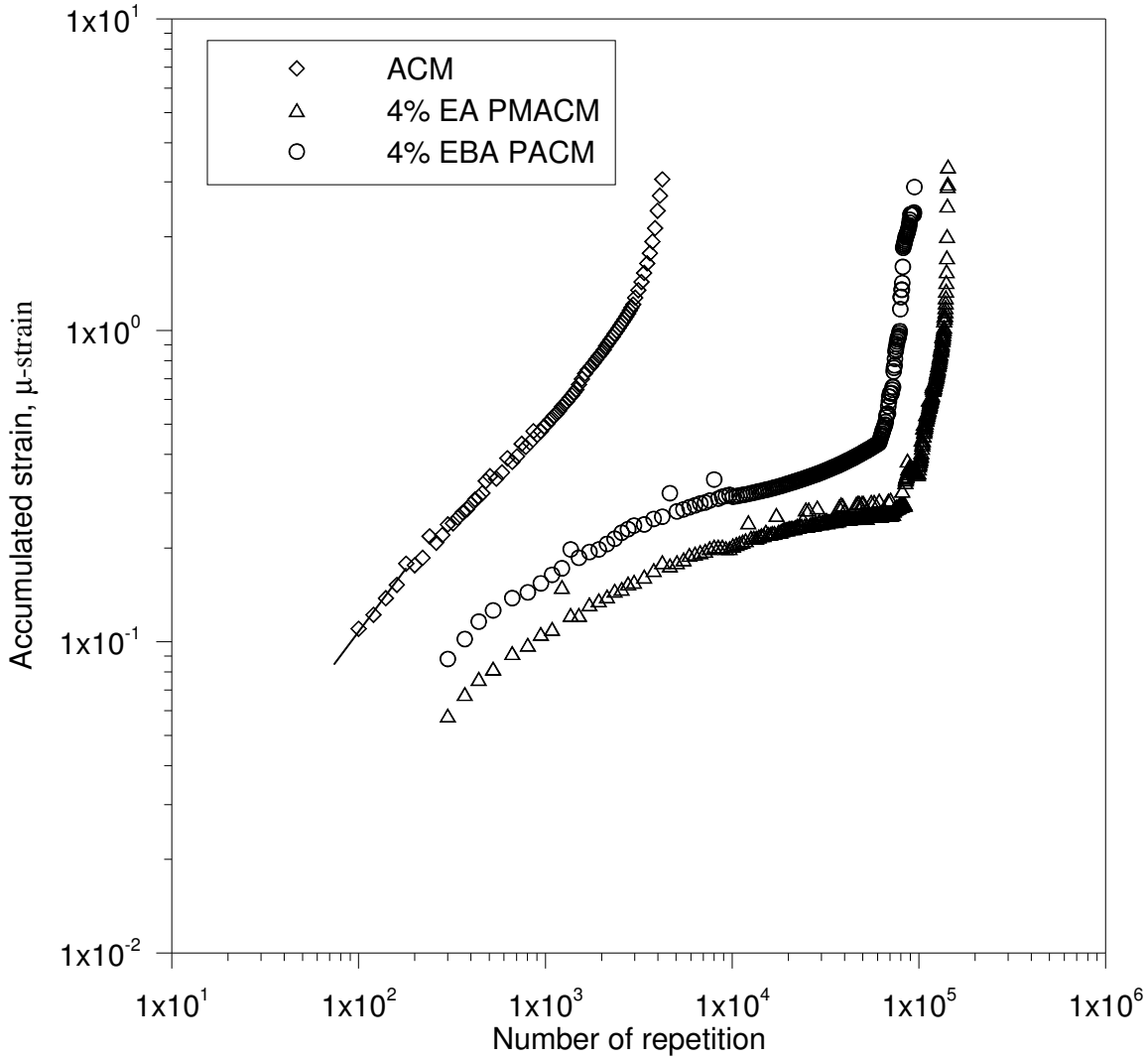

Figure 4.2.12: Rutting curve at 150 initial μ-strain and 50°C.

by the supplier. So, the overall performance of the high acrylate content EA-PMACM is superior to that of EBA in rutting resistance and Marshall Stability. However, M_R of EBA-PMACM was higher than that of EA-PMACM. The water stripping properties of the two polymers are comparable to that of ACM. In general, EBA showed better PMA properties, while EA displayed better ACM properties.

4.2.5. Conclusion

The influence of two different acrylate polymers on the modification of Arabian asphalt was investigated. In this study, polymer asphalt modification and concrete mix tests were performed. Ethylene acrylate copolymer and ethylene butyl acrylate terpolymer were used to modify asphalt and the performance of the two polymers was studied. The main difference between the two polymers is their acrylate content. The following conclusions are drawn on the basis of this investigation:

1) The addition of EA and EBA significantly increased the viscoelastic properties of the asphalt: G' and η' were considerably enhanced by the addition of any of the two polymers. EBA modified asphalt showed about twice the enhancement in rheological properties in comparison with EA. This ratio is the same as the ratio of the MFI of EA to that of EBA.

2) Both polymers reduce the temperature susceptibility of asphalt. Flow activation energy of asphalt was reduced from 114 to 101 and 106 kJ/mol due to addition of 4% of EA and EBA, respectively. Higher reduction in activation energy was obtained at higher polymer concentrations. The temperature susceptibility of two polymers is similar.

3) Both EBA copolymer and EA terpolymer modified asphalts showed acceptable storage stability results (< 20% difference in $|G^*|$) at 160^{o}C. However, EA-PMA was

found to have better storage stability PMA (9% difference in $|G^*|$) in comparison to EBA (16% difference in $|G^*|$). The storage stability results are in agreement with the predictions of the plots $\lambda^*H(\lambda)$ vs. λ, where a broader peak was obtained for EBA-PMA.

4) Both asphalt and PMA hardened due to ageing, with no or little influence on flow activation energy. Both polymers extended the window of upper service temperature. At the same polymer concentration, EBA-PMA showed higher upper service temperature (82^oC) than EA (76^oC). Moreover, both polymers satisfy the required PG.

5) Marshall stability test showed that both PMACMs retained a percent stability some what higher than that of ACM. Regardless of the polymer type, the influence of polymer modification on water sensitivity is not strong. The addition of the polymer didn't influence the water stripping properties of base asphalt and the percent loss was in the range 31-36%.

6) Polymer modification increased the value of M_R of asphalt concrete mix. The M_R of EBA-PMACM was the highest. Higher value of M_R indicates the less deformation at early life of the pavement. The resilient modulus of ACM followed the same trend as the elastic modulus of PMA.

7) Higher rutting resistance was obtained for PMACMs in comparison to ACM. Although the slope of the rutting curve is almost the same, accumulated deformation was smaller for EA-PMACM in comparison to EBA-PMACM. This implies the higher elastic behavior for EA-PMA. Endurance limit for EA-PMACM was significantly high among the concrete mixes.

8) EA (much cheaper than EBA) produced satisfactory properties of PMA and superior ACM properties when blended with the high asphaltenes Arabian asphalt.

4.2.6. References

1. F. J. Navarro, P. Partal, F. Martinez-Boza, C. Valencia, and C. Gallegos, *Chem. Eng. J.*, **89,** 53 (2002).
2. I. A. Al-Dubabe, H. I. Al-Abdul Wahhab, I. M. Asi, and M. F. Ali , *ASCE Mat..J.*, **10**, 161 (1998).
3. A. Adedeji, T. Grunfelder, F. S. Bates, C. W. Macosko, S. M. Gardiner, and Newcomb DE, *Polym. Eng. Sci.*, **36**, 1707 (1996).
4. X. Lu, and U. Isacsson, *Construction and Building Mat.*, **16,** 15 (2002).
5. A. A. Yousefi, A. Ait-Kadi, and C. Roy, *J. Mat. Civil Eng.*, **12**, 113 (2000).
6. P. J. Carreau, M. Bousmina, and F. Bonniot , *The Canadian J Chem. Eng.*, **78**, 495 (2000).
7. I. A. Hussein, M. H. Iqbal, and H. I. Al-Abdul Wahhab, *Rheologica Acta*, in press.
8. A. Ait-Kadi, B. Brahimi, and M. Bousmina, *Polym. Eng. Sci.*, **36**, 1724 (1996).
9. B. Sing, H. Tarannum, and M. Gupta, *J. Appl. Polym. Sci.*, **90**, 1365 (2003a)
10. B. Sing, H. Tarannum, and M. Gupta, *J. Appl. Polym. Sci.*, **90**, 1365 (2003b)
11. M. Murphy, M. O'Mahony, C. Lycett, and I. Jamieson, *J. Mat. Civil Eng.,* **13**, 306 (2001).
12. F. Bonemazzi, V. Braga, R. Corrieri, C. Giavarini, and F. Sartori F, *TRB*, **1535**, 36 (1996).
13. L. Zanzotto, J. Stastna, and K. Ho, *J. Appl. Polym. Sci*. **59**, 1897 (1996).
14. G. Polacco, O. J. Vacin, D. Biondi, J. Stastna, and L. Zanzotto, *Appl. Rheo.* **13**, 118 (2003).
15. A. A. Yousefi *J. Appl. Polym. Sci*., **90**, (2003).
16. J. Chen, M. Lio, and M. Shiah, *J. Mat. Civil Eng.*, **14**, 224 (2002).
17. G. Wen, Y. Zhang, Y. X. Zhang, K. Sun, andY. Z. Fan, *Polym. Testing,* **21**, 295 (2002a).
18. G. Wen, Y. Zhang, and Y. X. Zhang, *Polym. Eng. Sci.,* **42**, 295 (2002b).
19. H. Jin, G. Gao, Y. Zhang, Y. X. Zhang, K. Sun, and Y. Fan, *Polym. Testing*, **21**, 633 (2002).
20. A. H. Fawcett, and T. M. McNally, *Polymer,* **41**, 5315 (2000a).
21. A. H. Fawcett, and T. M. McNally, *J. Appl. Polym*. Sci., **76**, 586 (2000b)

22. A. H. Fawcett, and T. M. McNally, *Macr. Mat. Eng*., **286**, 126 (2001).
23. J. Stastna, L. Zanzotto, and O. J. Vacin, *J. Colloid and Interface Sci*., **259**, 200 (2003).
24. M. Panda, and M. Mazumder, *J. Mat. Civil Eng*., **14**, 527 (2002).
25. M. G. Baig, and H. I. A. Wahhab, *J. Mat. Civil Eng*., **10**, 153 (1998).
26. F. Parkar, and E. R. Brown, *ASTM Special Tech.. Publ.*, STP **1147**, 68 (1992).
27. C. Perdomo, J. W. Button , and R. L. Lytton, *ASTM Special Tech. Publ.*, STP **1147**, 295 (1992).
28. C. F. Berthelot, D. H. Allen, and C. R. Searcy, *J. Mat. Civil Eng.*, **15**, 496 (2003).
29. K. R. Hansen, G. Anderton, (1993), *ASTM Special Tech. Publ,,* STP **1193**, 69 (1993).
30. R. M. Anderson, D. E. Walker, and P. A. Turner, *Trans. Res. Rec.*, **1661**, 69 (1999).
31. J. L. Goodrich (1988), *Asphalt Paving Technology,* **57**, 116 (1988).
32. D. B. Knorr, R. R. Davison, and C. J. Glover, *Trans. Res. Rec.***, 1810**, 9 (2002).
33. A. H. El-Mubarak, S. Y. Sheikheldin, N. M. Fayad, and N. Khaja, *J. Environ. Sci. Health*, **A34**, 391 (1999).
34. I. A. Hussein, K. Ho, S. K. Goyal, E. Karbashewski, and M. C. Williams, *Polym. Degradation & Stability*, **68**, 381 (2000).
35. A. Zupancic, and M. Zumer, The Canadian J. Chem. Eng., **82**, 253 (2002).
36. H. U. Bahia, and R. Davies, *Proc. AAPT***, 63**, 414 (1994).
37. G. Gao, Y. Zhang, Y. X. Zhang, K. Sun K, and Y. Z. Fan, *Polym. & Polym. Composites*, **10**, 229 (2002).
38. H. Rassamdana, B. Dabir, M. Nematy, M. Farhani, and M. Sahimi (1996) *AIChE J*., **42**, 10 (1996).
39. H. U. Bahia, D. I. Hanson, M. Zeng, H. Zhai, M. A. Khatri, and R. M. Anderson, *NCHP Report 459*, National Academy Press, Washington D.C (2001).
40. P. Jew, J. A. Shimizu, M. Svazic, and R. T. Woodhams, (1986), *J. Appl. Polym. Sci.*, **31**, 2685 (1986).
41. J. B. Metcalf, K. Gopalakrishnan, and M. D. Waters, (2000), *Waste Management Series*, Waste Materials in Construction, 940 (2000).

42. A. Srivastava, P. C. Hopman, and A. A. A. Molenaar, *ASTM Special Tech. Publ.*, STP **1147**, 309 (1992).

4.3. Influence of Polymer Type and Structure on Polymer Modified Asphalt Concrete Mix.

4.3.1. Abstract

Two low density polyethylene (LDPE) resins and two ethyl vinyl acetate (EVA) polymers were used to modify asphalt. LDPE showed better elastic behavior in as received polymer, but higher elastic behavior was observed for EVA modified asphalt. Base asphalt concrete mix (ACM) and polymer modified asphalt concrete mix (PMACM) were prepared using Marshall Method of mix design (ASTM D 1559). Marshall Stability test, moisture susceptibility test (AASHTO T 283-89), resilient modulus (M_R) and permanent deformation test were performed to investigate the effect of polymer type and structure on PMACM. About 30% stability loss was observed for all concrete mixes. But EVA polymer with low VA content had the least stability loss (7%). Moisture susceptibility test revealed that ACM and PMACM were very sensitive to water. For all PMACMs, resilient modulus (M_R) was higher than that of ACM. Again, M_R was higher for EVA with low VA content. PMACM was found to have better permanent deformation (rutting) resistance compare to ACM. This resistance was significantly high for low VA content EVA mix, which indicated the excellent elastic behavior of this polymer in the mix. This elastic behavior of PMA correlates very well with the M_R and rusting resistance properties of PMACM.

4.3.2. Introduction

Although 4-6 wt% of asphalt is used with concrete, the asphalt binder improves the pavement performance significantly (Al-Abdul Wahhab et al., 1998). The most commonly observed types of distress in asphalt concrete pavements are rutting, fatigue cracking, low temperature cracking, ageing, raveling and stripping (Ait-Kadi et al., 1996; Wahhab et al., 1999; Lu et al., 1998; Yousefi et al., 2000; Carreau et al., 2000; Hussein et al., 2004).

Many investigations were performed on polymer modified asphalt (PMA), where asphalt is modified by different types of polymers. Goodrich (1988) related asphalt and PMA properties to the performance of asphalt concrete mix (ACM). The performance of PMA such as temperature susceptibility, force ductility; toughness-tenacity and low temperature ductility didn't correlate with the performance of the modified binders in mixes. Tests that involve very high strains didn't correlate conventional asphalt tests to the performance of ACM. Anderson et al., (1999) studied the relationship between low-temperature binder stiffness and ACM stiffness and poor correlation was reported. However, many reasearchers (Panda and Mazumder, 2002; Chen et al., 2004; Airey et al., 2004; Hansen and Anderton, 1993; Parker and Brown, 1992; Perdomo et al., 1992; Zoorob and Suparma, 2000; Zhou et al., 1997; Amirkhanian and Williams, 1993) investigated the properties of ACM and polymer modified asphalt concrete mix (PMACM), and the improvement in the performance of concrete mixes were compared. Modeling of ACM behavior like viscoelastic properties, permeability etc. were also performed (Berthelot et al., 2003; Krishnan and Rao, 2001).

Murphy et al., (2001) modified asphalt using recycled polymers like polyethylenes, polypropylenes, polyetherpolyurethane and rubber. The performance was evaluated by measuring viscosity, penetration, softening point, ageing and rheology. Moreover, ACM tests like indirect tensile stiffness and rutting resistance were performed. It was found that the rutting performance appeared to reproduce the binders melt rheology (Murphy et al., 2001).

In a recent publication (Hussein et al., in press), our group studied the influence of the M_W of low density polyethylene (LDPE) and vinyl acetate (VA) content of EVA on the properties of PMA. It was found that EVA with low VA content (19.5 wt%) showed the best storage stability and reduced temperature susceptibility. Also, EVA modified asphalt extended the window of the performance grading (PG) and improved viscoelastic behavior of base asphalt. In addition, the influence of the M_W of LDPE on the properties of PMA was studied. The previous study focused on the influence of polymer type abd structure on the properties of PMA.

In this study, the effect of polymer type and structure on PMACM was investigated. Marshall Method of mix design was used to prepare sample and performance was compared. The Marshall Stability test, stripping test, resilient modulus and permanent deformation measurements were used to correlate the properties of PMA to that of PMACM. The influence of M_W of low density polyethylene (LDPE) and the vinyl acetate (VA) content of ethylene vinyl acetate (EVA) on the properties of PMACM was investigated. Here, the consequences of polymer modification of their ACM are studied.

4.3.3. Experimental

Material

Two LDPEs of different M_w and two EVA polymers of different VA contents were used to modify asphalt. This modification was done with 4% polymer as this concentration satisfied the required PG (76-10) in the Gulf region (Hussein et al., in press). The PG was evaluated according to Strategic Highway Research Program (SHRP) specification. Table 4.3.1 shows the properties of the polymers used in this study as well as the PG for asphalt & PMAs. The polymer resins were supplied by ExxonMobil, Belgium. Supplier data are presented in Table 4.3.1. Also, weight average molecular weights (M_w) and molecular weight distribution (MWD) are reported. The details of polymer characterization are given elsewhere (Hussein et al., in press). Asphalt of PG 64-22 was used in this study. The asphalt was obtained from Saudi Aramco Riyadh Refinery. Low M_w LDPE was labeled as LDPE1 and the high M_W LDPE as LDPE2. On the other hand, EVA with 19 wt% VA content was represented by label 1 and the 27.5 wt% VA content of EVA by label 2. The two EVA resins had the same MFI. Aggregates, used to prepare mix samples, were obtained from local sources.

LDPE1 mix and EVA1 mix were selected to study the effect of polymer type since their MFI were similar (see Table 4.3.1).

PMA Sample Preparation

To analyze the melt rheology of asphalt and PMA, disc samples were prepared for frequency sweep in Advanced ARES rheometer. Sample preparation and test procedure were described elsewhere (Hussein et al., in press).

Table 4.3.1: Characterization of polymers

Polymer	**Density (g/cm^3)**	**Melting Point (^oC)**	**MFI (g/10min)**	**M_W (kg/mol)**	**MWD**	**PG (asphalt + 4% of corresponding polymer)**
LDPE1	0.913	100	155	71.92	9.75	76-16
LDPE2	0.913	100	70	102.93	12.4	76-10
EVA1	0.938	81	150	45.63	4.71	82-10
EVA2	0.950	68	150	40.48	5.4	76-22

Mix Design

The mix design was done according to Marshall Method (ASTM D 1559) of mixed design. Wearing course was used as mix code. Table 4.3.2 shows the details of the mix design for base asphalt mix and similar design was used for PMACM. The standard cylindrical shaped Marshall specimen of 100 mm × 62.5 mm was prepared for ACM and PMACM. The prepared specimens were used for the following measurements.

Marshall Stability test

Stability is the most important property of the bitumen mixture in the wearing course design. It shows the ability to resist shoving and rutting under traffic (Hınıslıoğlu and Ağar, 2004). Marshall Stability test of ACM and PMACM was performed in a Marshall testing Machine at a constant rate of 51 mm/min. Details of sample preparation are given elsewhere (Iqbal et al., 2004). The obtained load was multiplied by a stability correlation ratio to calculate the correct load. Average load and percent difference in load were reported for the initial and final condition.

Moisture Susceptibility Test (Lottman Test, AASHTO T-283-89)

Moisture susceptibility was evaluated by determining the changes in the mechanical properties of the specimens after conditioning. This test reveals the resistance of compacted bituminous mixture to moisture induced damage. It is done by measuring the change of diametral tensile strength resulting from the effects of saturation and accelerated water conditioning of compacted asphalt mixtures in the laboratory. The results may be used to simulate the long-term stripping susceptibility of the asphalt mixtures. Details about sample preparation are given elsewhere (Iqbal et al., 2004).

Table 4.3.2: Mix Design

	Job Mix Formula (JMF)	**Specification Limits**
1. Optimum Asphalt Content, % (60/70 Pen grade asphalt)	5.3	5.3 +/- 0.3
2. Aggregate Grading: % Passing		
1"	100	100
3/4"	87	80 - 95
# 4	55	48 - 62
# 10	38	32 - 45
# 40	21	16 - 26
# 80	13	8 - 18
# 200	6	4 - 8
3. Marshall Test Results (75 blows, compaction temperature 150^{o}C)		
Stability (Kg)	1804	800 Min.
% Air Voids. Total Mix	4.4	4.0 - 6.0
Flow (mm)	3.2	2.0 - 4.0
% Voids filled w/asphalt	74	70 - 80
Stability Loss, (%)	16.2	20 Max.
Void in Mineral Aggregates (VMA)	16.04	-

Samples were conditioned in water for 2 hours at room temperature. The load (indirect tensile strain, ITS) was applied on the specimen at a constant deformation rate of 51 mm per minute and the load at failure was obtained. For the final condition, specimens were placed in vacuum and in water at 60^{o}C for 24 hours, then at room temperature for 2 hours. The average difference in ITS between the final and initial conditioning was obtained.

Resilient Modulus, M_R, (ASTM D 4123)

Diameter resilient modulus is the most important variable to mechanistic design approaches for pavement structures. It is the measure of pavement response in terms of dynamic stresses and corresponding strains. A static load of about 10 lb was applied to hold the specimen in place. A dynamic load in the linear range was applied with a frequency of 1 Hz, and the resulting horizontal deformation was obtained at 50^{o}C.

Permanent Deformation (Rutting)

To analyze the performance of asphalt concrete mix, permanent deformation, measured by indirect tensile testing method, is both practical and versatile (Baig and Al-Abdul Wahhab, 1998). Permanent deformation measurements were performed on ACM and PMACM at 50^{o}C. The load was used for 150 initial μ-strain deformations. Deformation due to applied repeated load was obtained until the failure of the specimen. Details of the rutting test are given elsewhere (Iqbal et al., 2004)

4.3.4. Results and Discussions

Melt Rheology

In Figure 4.3.1, storage modulus, G′, of PMA is shown for 4 wt% polymer concentration. Also, base asphalt was shown for comparison purposes. Addition of

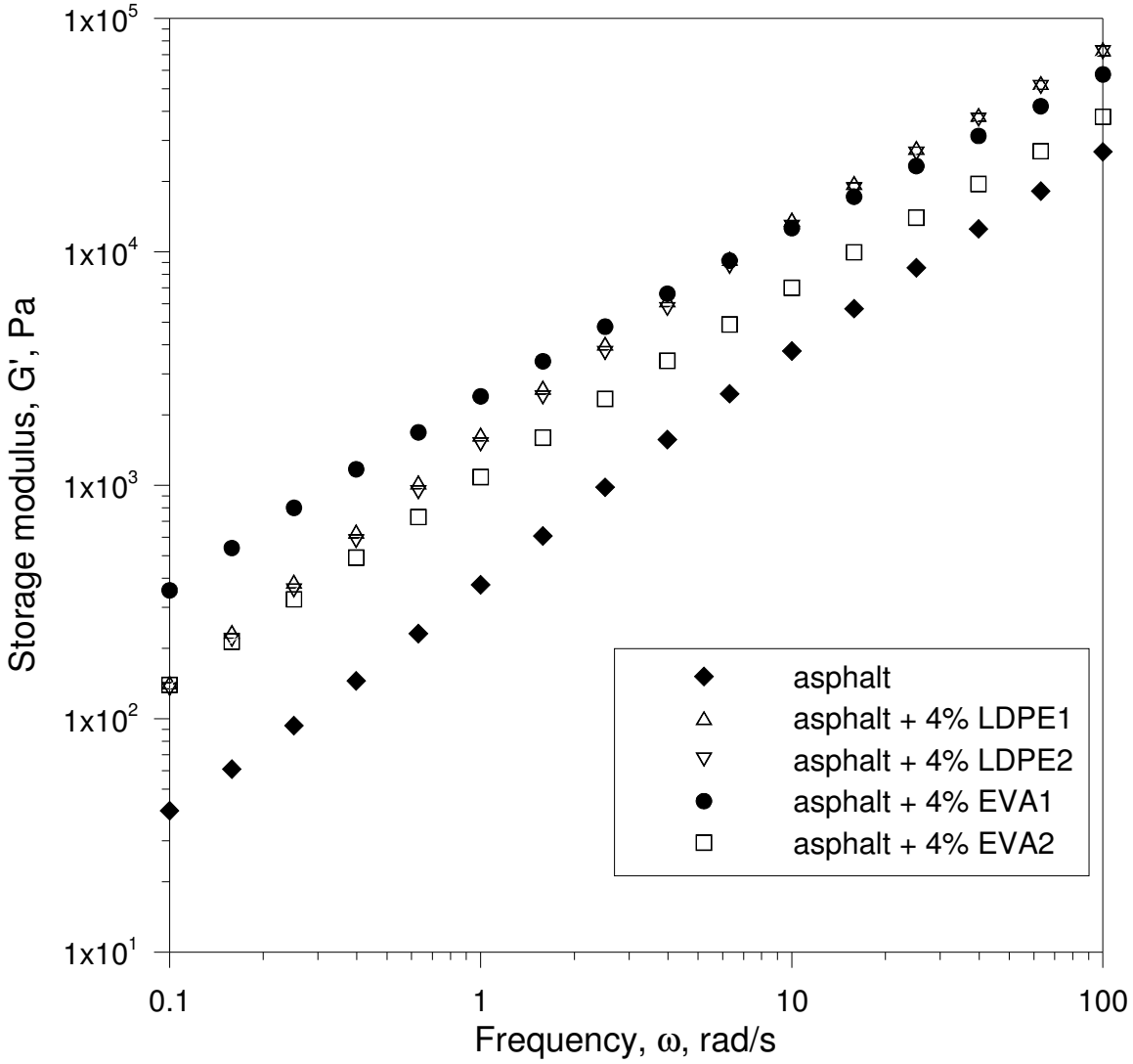

Figure 4.3.1: G′(ω) of asphalt and PMAs (T_{test} = 50°C).

polymers increased G′ value of base asphalt. The highest increase was obtained for EVA1 modified asphalt. At low ω, LDPEs and EVA2 PMAs showed similar G′(ω) values.

Marshall Stability Test

The results of the required compressive loads to break specimens in Marshall Stability test are presented in Table 4.3.3. Three samples were used to obtain the average load and the corresponding standard deviations were reported. The percent stability losses due to conditioning were 34%, 30%, 32%, 7% and 32% for ACM, LDPE1, LDPE2, EVA1 and EVA2 concrete mixes, respectively. It can be observed that the initial stability for ACM was higher than PMACM. All PMACMs showed similar initial stability except EVA1 mix, which showed the least stability loss (7%). The percent stability loss was the highest for ACM and the least for EVA1-PMACM. No significant difference in percent stability loss was observed between LDPE1 and LDPE2. So, increasing M_w from 72 to 102 kg/mol effect on the stability of LDPE modified concrete mix. EVA1 mix showed remarkable stability in comparison with EVA2. The reason is likely the low amount of VA present in EVA. EVA with high VA content has a rigid long molecule which is not compatible with asphalt's constituents as discussed in a previous publication (Hussein et al., in press). Comparison between polymer types (LDPE1 vs. EVA1) suggests that the polymer type has influenced the Marshall Stability. The low VA polymer forms a continuous phase with asphalt as suggested by their rheology (Hussein et al., in press). Also, EVA1 might have influenced the interfacial and adhesion properties of PMA and concrete.

Table 4.3.3: Marshall Stability test.

Sample ID	Stability	Sample No	Load (kN)	Average Load (kN)	Standard Deviation
ACM	Initial	1	20.22	19.81	0.41
		2	19.64		
		3	19.58		
	Final	1	11.61	13.15	1.39
		2	14.32		
		3	13.53		
LDPE1-PMACM	Initial	1	16.49	15.33	1.27
		2	14.69		
		3	14.82		
	Final	1	10.06	10.66	0.53
		2	10.82		
		3	11.10		
LDPE2-PMACM	Initial	1	15.55	14.40	2.03
		2	12.68		
		3	14.98		
	Final	1	10.85	9.74	1.20
		2	9.92		
		3	8.45		
EVA1-PMACM	Initial	1	14.52	14.71	0.99
		2	14.67		
		3	14.95		
	Final	1	12.85	13.70	0.94
		2	12.01		
		3	13.26		
EVA2-PMACM	Initial	1	16.62	15.19	2.02
		2	13.76		
		3	14.95		
	Final	1	10.53	10.37	0.17
		2	10.19		
		3	10.38		

Moisture Susceptibility Test

The initial and final ITS values were presented in Table.3.4.4. The average ITS value for three specimens is showed along with the standard deviation. The percent losses due to the conditioning were 38%, 64%, 43%, 23% and 48% for ACM, LDPE1, LDPE2, EVA1, and EVA2 mixes, respectively. ACM and all PMACMs showed almost similar initial ITS. However, the percent loss in ITS value was higher for PMACMs in comparison to ACM except EVA1 mix. Addition of polymer makes asphalt structure more complex (Stastna et al., 2003; Gao et al., 2002). LDPE may have physical bond only with asphalt phase. No network behavior or crosslinking is expected form such a saturated polymer. When vacuum was applied and specimens were kept at high temperature, it is likely that specimens were almost saturated with water. In this case, physical bonding between PMA and concrete is expected to weaken; resulting in a significant loss in ITS. Also, these results show that low M_w LDPE is highly water sensitive and high M_w LDPE is better. The previous rheological results suggest that LDPE2 forms better homogeneous mixture with asphalt than LDPE1. EVA1 showed excellent network behavior in PMACM and sustained the conditioning. So, the moisture susceptibility is linked to the miscibility of their PMA. The performance of EVA2 was poor and comparable to that of LDPEs. This supports the loss of polymer due to stripping and indicates the water sensitivity of high VA content EVA modified asphalt. In comparison of polymer type, EVA1 showed better resistance to moisture induced damage than that of LDPE1. A correlation of water susceptibility and polymer miscibility was observed.

Table 4.3.4: Moisture sensitivity test (Lottman Test).

Sample ID	Condition	Sample No.	Load (kN)	Average Load (kN)	Standard Deviation
ACM	Initial	1	10.74	10.77	0.02
		2	10.77		
		3	10.82		
	Final	1	6.37	6.69	4.05
		2	7.73		
		3	5.98		
LDPE1-PMACM	Initial	1	10.48	10.07	0.34
		2	10.00		
		3	9.90		
	Final	1	3.45	3.60	0.32
		2	3.98		
		3	3.38		
LDPE2-PMACM	Initial	1	9.63	9.50	0.20
		2	9.36		
		3	9.50		
	Final	1	5.99	5.39	1.12
		2	5.92		
		3	4.28		
EVA1-PMACM	Initial	1	10.52	10.88	0.21
		2	10.22		
		3	10.96		
	Final	1	8.12	8.41	0.50
		2	8.82		
		3	8.31		
EVA2-PMACM	Initial	1	11.76	11.31	0.70
		2	10.77		
		3	11.40		
	Final	1	4.85	5.85	1.12
		2	7.07		
		3	5.63		

Resilient Modulus, M_R

Figure 4.3.2 shows the resilient modulus of ACM and PMACM at 50°C. It was observed that M_R for PMACM was higher than that of ACM. These results are in agreement with previous reports (Jew et al., 1986; Metcalf et al., 2000). Among the two LDPEs, LDPE2 (high M_w) showed a higher increase in resilient modulus than LDPE1. This result suggests that polymer with high molecular weight exhibits high stiffness which is quite normal. On the other hand, EVA1 increased this modulus significantly in comparison to EVA2, which is a consequence of its high G′ modulus (see Figure 4.3.1). Moreover, additi0on of EVA1 showed the highest increase in M_R value. From this point of view, EVA with low VA content is superior over LDPE. These results correlate very well with the G′ data of these polymers, where the trend was qualitatively similar. So, screening of polymer for their M_R values could be obtained from simple measurement of G′.

Permanent Deformation (Rutting)

Figure 4.3.3 displayed the accumulated strain vs. repeated load at 150 initial μ-strain and 50°C. At low repeating loads, there was no significant difference in deformation between ACM and PMACMs. But this difference was distinguishable at high load repetitions. ACM showed higher permanent deformation than PMACMs. Similar findings were reported in previous studies (Srivastava et al., 1992; Baigh and Al-Abdul Wahhab, 1998). Regardless of the major difference in M_w of the two LDPEs, their rutting resistance is comparable. These results are in agreement with their G′ data, where the two resins showed very similar values for G′(ω) (see Figure 4.3.2). So, the G′ data of LDPEs directly correlates with the rutting resistance of their asphalt concrete mix. The

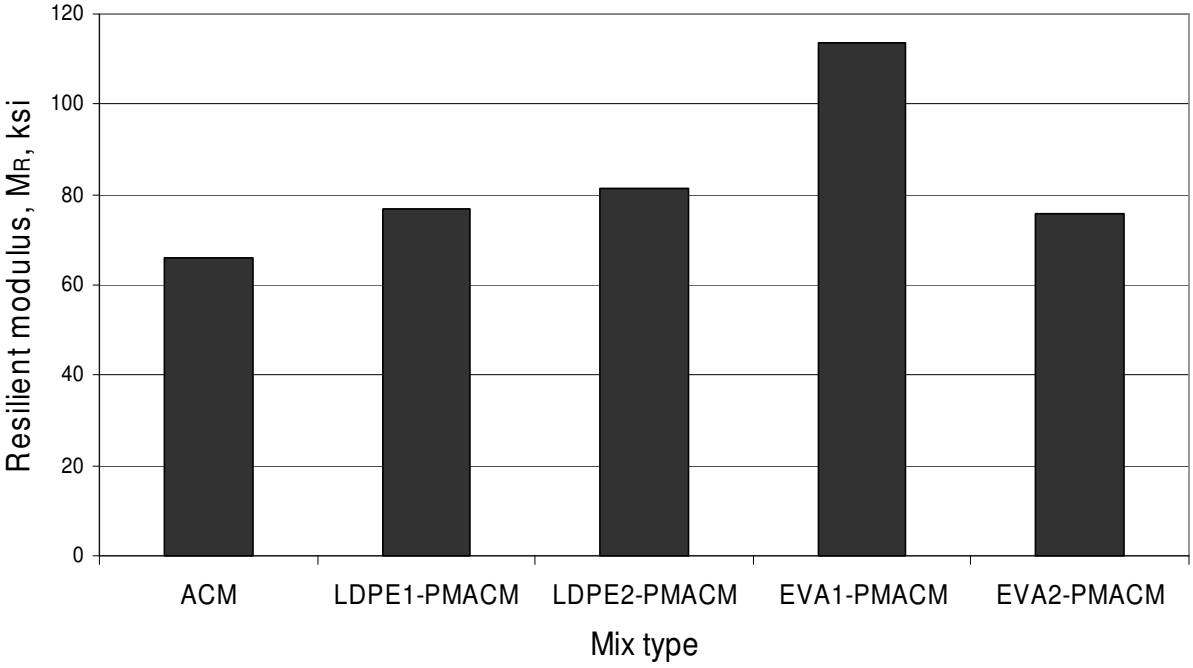

Figure 4.3.2**:** Resilient modulus for ACM and PMACMs @ 50^{o}C

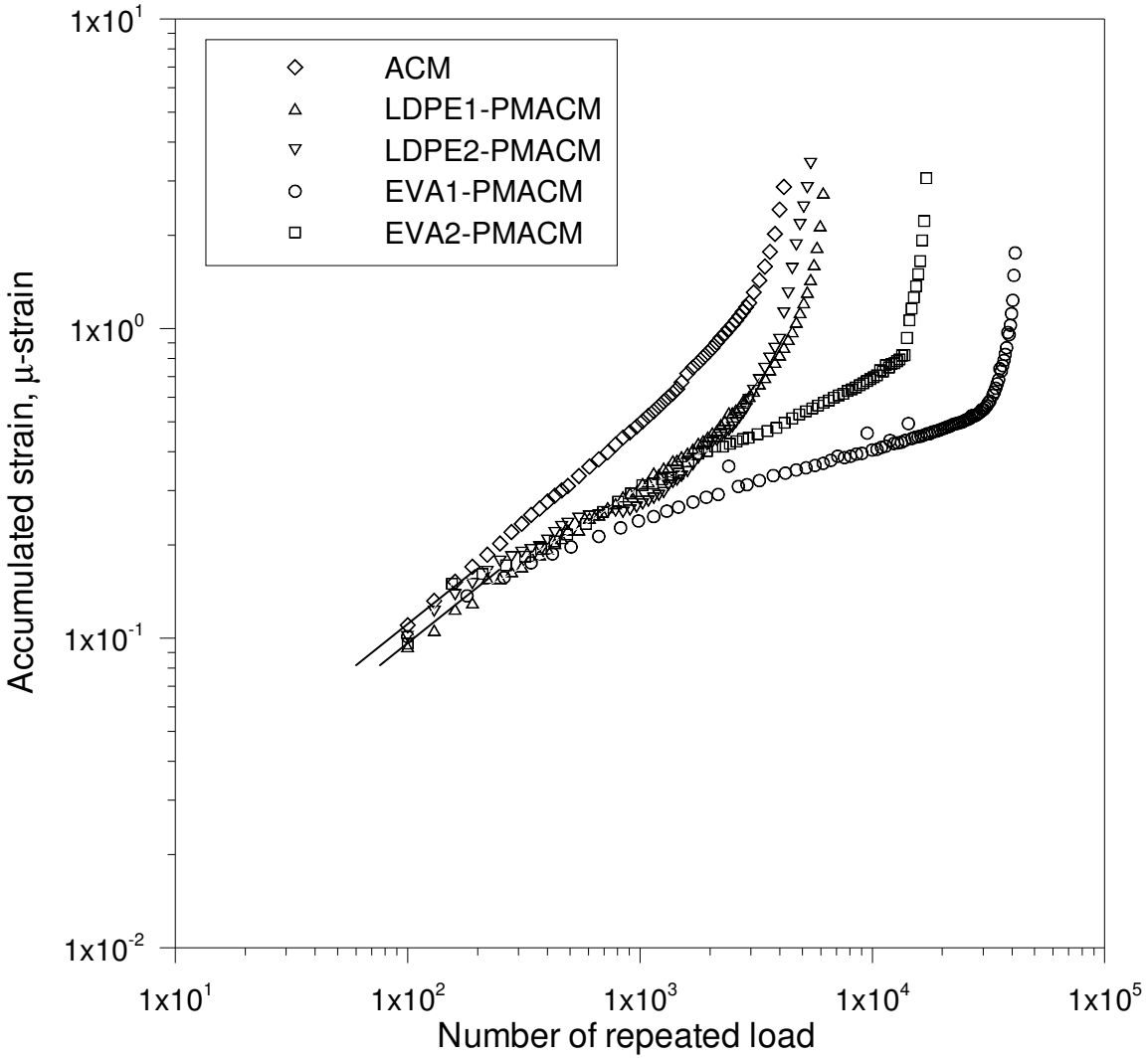

Figure 4.3.3: Rutting curve at 150 □-strain @ 50°C

data at low loads is approaching the same limiting values. So, the behavior of all polymers at low load is similar. Table 4.3.5 shows the slope and the anti-log on the intercept of each curve at low repeated load.

Both EVA modified asphalt mix showed better rutting resistance behavior in comparison to LDPE modified asphalt mix. EVA1 modified asphalt mix showed the best resistance for rutting. The significant improvement in rutting for EVA1 mix expresses the excellent elastic behavior in concrete mix. This behavior is in direct agreement with its G′ data shown in Figure 4.3.1. Again, there exists a correlation between the G′ of PMA and the rutting resistance of its concrete mix. Figure 4.3.1 expressed that EVA1-PMA showed the highest storage modulus (elasticity) at the low ω. At low ω, EVA2-PMA's elasticity was similar to LDPE-PMA. But the trend showed that at the lowest ω (<0.1rad/s) EVA2-PMA would show higher elasticity compared to LDPE-PMA. So, less deformation for EVA2-PMACM was observed in rutting test compared to LDPE-PMACMs. EVA2 rutting resistance was less than EVA1. Hence, low VA is favored over high VA content polymers for PMACM. With the same MFI (~150), EVA1 showed less permanent deformations in comparison to LDPE1.

Most interesting behavior was observed at higher number of repeated loads. At these loads, ACM failed gradually compare to PMACMs. Due to the presence of vinyl group, EVA is more rigid than LDPE. Hence, sudden failure was most likely and was found for EVA ACM. EVA2 mix showed rapid failure compared to EVA1 mix. This indicates that high VA content makes concrete mixes more brittle at higher stress. So, polymer structure and the rigidness of the molecular directly correlate with its ultimate accumulated strain. At large strains, the rheology of polymers is usually very sensitive to

Table 4.3.5: Rutting Coefficients

Mix Type	**Anti log of intercept**	**Slope**	**R^2**
ACM	0.0045	0.6876	0.9957
LDPE1-PMACM	0.0082	0.5277	0.997
LDPE2-PMACM	0.0123	0.4635	0.975
EVA1-PMACM	0.037	0.2657	0.9686
EVA2-PMACM	0.0188	0.3957	0.987

molecular structure (stray flow). Also, the poor compatibility between asphalt and EVA is likely to contribute to the failure of ACM at high loads.

Endurance limit of ACM and PMACM were shown in Figure 4.3.4. PMACM showed higher endurance limit compared to ACM. Endurance limit for EVA1 modified asphalt concrete mix was significantly high among all the mixes. Accumulated deformation was less for EVA1 mix (Figure 4.3.3) and more than 4×10^4 cycles were needed to break the concrete mix. This shows that EVA1 asphalt concrete mix is both strong and tough. On the other hand, EVA polymers are better than LDPE of similar rheological characteristics. So, asphalt modified with EVA with low VA content had superior properties in both PMA and PMACM.

4.3.5. Conclusion

In this study, two LDPE polymers of different MFI and two EVA polymers of different VA contents were used to modify asphalt. This modification was performed with a 4% polymer concentration. Marshall Method of mix design was used to prepare the asphalt concrete mix. The followings are the conclusions of this study.

1) Marshall stability was obtained and the percent stability loss due to conditioning was measured for ACM and PMACM according to ASTM D 1559. Although ACM showed the highest initial stability but its stability loss was the highest in comparison to other mixes. Stability loss was the lowest for EVA1 asphalt concrete mix (7%). In all other concrete mixes the loss was about 30%.

2) Moisture susceptibility test showed that both ACM and PMACMs are water sensitive. The percent loss in ITS due to moisture induced damaged for PMACM and ACM were comparable and in the range of 31-36%.

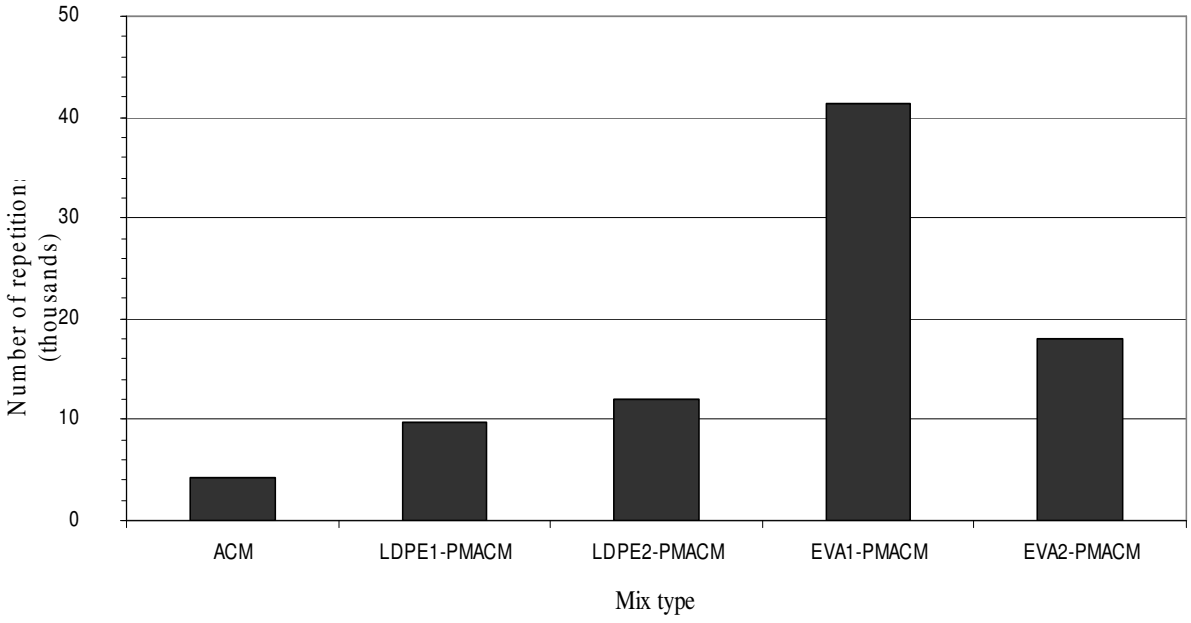

Figure 4.3.4**:** Endurance limit

3) Polymer modification increased the M_R of base asphalt. Low Mw LDPE-PMACM showed lower M_R compared to high Mw LDPE mix. For EVA, the resin with high elastic modulus showed a higher M_R.

4) Rutting behavior of PMACM has improved significantly over that of base asphalt. Accumulated deformation was very small for EVA1-PMACM. It is likely that the homogeneity of EVA1 has also played a role, especially at high loads. In general, EVA concrete mixes showed less deformation than that of LDPE concrete mixes. Endurance limit was significantly high for EVA1 modified asphalt concrete mix. However, all PMACMs showed higher endurance limit in comparison to ACM.

5) ACM showed gradual failure at higher number of repeated loads in comparison to PMACMs. At higher number of repeated stress, both LDPE PMACMs showed gradual breakdown compared to EVA PMACMs. For LDPE ACM, LDPE1 and EVA mix showed gradual failure. More than 4×10^4 cycles were needed before the failure of EVA mix. So, EVA1 asphalt modification has resulted in a strong and tough ACM.

6) Permanent deformation by repeated load is a solid state rheology. The remarkable finding of this study is the relation between melt rheology ($G'(\omega)$) and solid state rheology (rutting test). Permanent deformation test is the most practical test. But, the similar properties can be qualitatively predicted from melt rheology i.e. Rheological testing of PMA could be sufficient to screen different polymers without doing mix test. For the same polymer, the ratio of the elastic moduli in the PMAs was found to be about the same as their endurance limits. However, for different polymers, the relation doesn't hold as observed for EVA and LDPE polymers.

In brief, low VA content EVA blend with asphalt adheres to concrete very well, gives less stability loss, higher resilient modulus and excellent rutting resistance. All of these make EVA with low VA content superior to LDPE.

4.3.6. References

1. Airey G. D., Rahimzadeh B., and Collop A. C., (2004), "Linear Rhelogical Behavior of Bituminous Paving Materials", *Jouranl of Materials in Civil Engineering,* V. 16(3), pp. 212-220.
2. Al-Dubabe I.A., Al-Abdul Wahhab H.I., Asi I.M., and Ali M.F. (1998), "Polymer Modification of Arab Asphalt", *ASCE Material Journal*, V. 10(3), pp: 161-167.
3. Ali M., Al-Abdul Wahhab H.I., Asi I. and Al-Dubabe I. (1999), "Characterization of Polymer Modified Gulf Asphalts", *Petroleum Science and Technology*, V.17(1, 2), pp: 125-146.
4. Ait-Kadi A., Brahimi B., and Bousmina M. (1996), "Polymer Blends for Enhanced Asphalt Binders", *Polymer Engineering and Science*, V.36. No.12, pp: 1724-1733.
5. Amirkhanian S. N., and Williams B., (1993), "Recyclablity of Moisture Damaged Flexible Pavements", *Journal of Materials in Civil Engineering,* V.5(4), pp. 510-530.
6. Anderson R. M., Walker D. E., Turner P. A., (1999), "Low-Temperature Evaluation of Kentucky Performance-Graded 70-22 Asphalt Binders", *Transportation Research Record*, 1661 (Hot-Mix Asphalt Binders), pp: 69-74.
7. Baig M. G., and Al-Abdul Wahhab, H. I., (1998), "Mechanistic Evaluation of Hedmanite and Lime Modified Asphalt Concrete Mixtures", *Journal of Materials in Civil Engineering,* V. 10(3), pp. 153-160.
8. Berthelot C. F., Allen D. H. and Searcy C. R., (2003), "Method for Performing Accelerated Characterization of Viscoelastic Constitutive Behavior of Asphalt Concrete", *Journal od Materials in Civil Engineering,* V. 15(5), pp. 496-505.
9. Carreau P. J., Bousmina M., and Bonniot F., (2000), "The viscoelastic properties of Polymer-Modified Asphalt", *The Canadian Journal of Chemical Engineering*, V.78, No.3, pp: 495-502.
10. Chen J., Lin K., Young S., (2004), "Effects of Crack Width and Permeability on Moisture-Induced Damage of Pavements", *Journal of Materials in Civil Engineering,* V. 16(3), pp. 276-282.
11. Gao Gt, Zhang Y, Zhang YX, Sun K, Fan YZ (2002) Improved Storage Stability of LDPE/SBS Blends Modified Asphalt. Polym & Polym Comp*,* 10(3): 229-236.
12. Goodrich J. L., (1988), "Asphalt and Polymer Modified Asphalt Properties Related to the Performance of Asphalt Concrete Mixes", *Asphalt Paving Technology,* V.57, pp: 116-175.
13. Hansen K. R., Anderton G., (1993), "A Laboratory Evaluation of Recycled Tire Rubber in Hot-Mix Asphalt Paving Systems", *ASTM Special Technical Publicaiton,* STP 1193, pp. 69-83.

14. Hınıslıoğlu S., and Ağar E., (2004), "Use of Waste High Density Polyethylene as Bitumen Modifier in Asphalt Concrete Mix", *Materials Letter,* V. 58, pp. 267-271.
15. Iqbal M. H., (2004), "Influence of Polymer Type and Structure on the Modification of Saudi Asphalt", *MS Thesis,* KFUPM, Dhahran, Saudi Arabia
16. Jew P., Shimizu J. A., Svazic M., and Woodhams R. T., (1986), "Polyethylene-Modified Bitumen for Paving Applications" *Journal of Applied Polymer Scinence,* V. 31, pp.2685-2704.
17. Krishnan J. M., and Rao C. L., (2001), "Permeability and Bleeding of Asphalt Mixture using Theory" *International Journal of Engineering Science,* V. 39, pp. 611-627.
18. Lu X., and Isacsson U., (1998), "Effect of Filler on Low Temperature Physical Hardening of Bitumen", *Construction and Building Materials,* V.12, pp: 463-470.
19. Metcalf J. B., Gopalakrishnan K., and Waters M. D., (2000), "An Initial Investigation of the Rubber Waste (EPDM) in Asphalt Concrete Mixtures", *Waste Management Series,* Waste Materials in Construction, pp. 940-952.
20. Murphy M., O'Mahony M., Lycett C., and Jamieson I., 2001, "Recycled Polymers for Use as Bitumen Modifiers", *Journal of Materials in Civil Engineering*, V. 13(4), pp: 306-314.
21. Panda M., and Mazumder M., (2002), "Utilization of Reclaimed Polyethylene in Bituminous Paving Mixes", *Journal of Materials in Civil Engineering,* V. 14(6), pp. 527-530.
22. Parkar F., Brown E. R., (1992), "Effects of Aggregate Properties on Flexible Pavement Rutting in Alabama", *ASTM Special Technical Publication*, STP 1147, pp. 68-89.
23. Perdomo C., Button J. W., and Lytton R. L., (1992), "A New Approach for Prediction of Permanent Deformation", *ASTM Special Technical Publication,* STP 1147, pp. 295-309.
24. Romero P., Youtcheff J. and Stuart K., (1999), "Low-Temperature Physical Hardening of Hot-Mix Asphalt", *Transportation Research Record*, 1661 (Hot-Mix Asphalt Binders), pp: 22-26.
25. Srivastava A., Hopman P. C., and Molenaar A. A. A., (1992), "SBS Polymer Modified Asphalt Binder and its Implication on Overlay Design", *ASTM Special Technical Publication,* STP 1147, pp. 309-329.
26. Stastna J, Zanzotto L, Vacin O J (2003) Viscosity Function in Polymer Modified Asphalt. J Colloid and Interface Sci 259(1): 200-207.
27. Yousefi A. A., Ait-Kadi A., and Roy C., (2000), "Composite Asphalt Binders: Effect of Modified RPE on Asphalt", *Journal of Materials in Civil Engineering*, V.12, No.2, pp: 113-123.
28. Zhou H., Nodes S. E., and Nichols J. E., (1997), "Evaluation of Three Polymer Modified Asphalt Concretes", *Materials and Construction*, Transportation Research record, No.1454, pp: 181-192.
29. Zoorob S. E., and Suparma L. B., (2000), "Laboratory Design and Investigation of the Properties of Continuously Graded Asphaltic Concrete Containign Recycled Plastics Aggregate Replacement (Plastiphalt)", *Cement & Concrete Composites,* V. 22, pp. 233-242.

Chapter 5

CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The influence of polymer type like LDPE, EVA and acrylate grafted polymer, and molecular parameters such as M_w of LDPE, VA content of EVA, and acrylate content of acrylate grafted polymers on the modification of asphalt were investigated. Two LDPE of different M_w and two EVA of different VA content were compared to observe the effect of polymer structure on the asphalt modification. LDPE and EVA of similar MFI (~150) were compared to study the effect of polymer type. Also, the influence of M_w of LDPE on asphalt modification was examined. Two acrylate grafted polymers of different acrylate group content (ethyl and butyl) were used to examine the influence of alkyl acrylate content on the modified asphalt. In addition, the effect of polymer concentrations was studied by modifying asphalt with three different concentrations (4, 6 and 8%).

Several rheological measurements and data treatment approaches were used to observe the viscoelastic behavior of base asphalt and PMA. First, frequency sweep was done to observe the change in viscoelastic behavior of base asphalt due to polymer modification. Base asphalt was also treated under similar condition for comparison purposes. Flow activation energy of base asphalt and PMA was obtained by using

Arrhenius equation. Storage stability of PMA was performed in enhanced storage conditions. Artificial ageing techniques were used to simulate the ageing and rheological properties were compared with unaged ones. Moreover, performance grading was done for the PMA which satisfied SHRP specification. Polymer modified asphalt concrete mix (PMACM) was used to perform different tests and the improvement was cross checked with PMA behavior.

To avoid structural damage of polymer and asphalt, optimum blending time was used. Polymer modification significantly improved the viscoelastic properties (G', η') of the asphalt. This improvement was high with the polymer concentrations. LDPE with high M_w improved rheological properties higher than that of LDPE with low M_w. On the other hand, EVA with low VA content was found to improve rheological properties higher than that of EVA with high VA content. For the comparison of EVA and LDPE, EVA with low VA content showed better performance in PMA. EVA decreases the flow activation energy of base asphalt. Reduction of flow activation energy reduces the degree of temperature sensitivity. As a result, temperature susceptibility of PMA is reduced. This reduction was high at higher EVA content. LDPE increased the flow activation energy of base asphalt. Storage stability of LDPE modified asphalt showed the least variations. EVA with low VA content showed good storage stability. Artificial ageing enhances the loss of smaller molecules and generation of free radicals which x-link with other constituents of asphalt. EVA PMACM with low VA content was found to have less stability loss. Both ACM and PMACM were found to be water sensitive. The percent loss of ITS was high for LDPE with low M_w. PMACM showed better rutting resistance in comparison to ACM and excellent rutting resistance was obtained for EVA with low VA

content. Also, this behavior was reflected in the endurance limit. Endurance limit of EVA PMACM was high and it was the highest for EVA with low VA content. A correlation was obtained between the melt state (PMA) rheology, and the resilient modulus and rutting properties of PMACM. Polymer, which showed higher elastic behavior in modified asphalt, showed better rutting resistance behavior in the asphalt concrete mixes provided that the melting point of the polymer should be higher than the examined temperature.

The addition of grafted polymer (EA and EBA) significantly changed the rheological behavior of asphalt. EBA was found to improve viscoelastic behavior of asphalt higher than that of EA. Both polymers were found to decrease the flow activation energy of asphalt and reduction was higher with higher polymer concentration. Moreover, excellent storage stability and improved PG were observed for the acrylate polymers. Both polymers showed improved mix properties. Higher percent retained stability, higher value of resilient modulus and excellent rutting resistance were observed for acrylate polymer modified asphalt concrete mix. This improvement was higher for EA concrete mix compared to EBA modified asphalt concrete mix. However, no significant improvement was observed in the case of water sensitivity.

5.2. Recommendations for Future Work

LDPE is cheap and has good storage stability. But it doesn't show any x-linking or network behavior in the asphalt phase. It is recommended to modify LDPE and then use functionalized LDPE in PMA. Also, the influence of asphaltene content on polymer modification should be examined. In addition, the effect of weather conditions (natural and accelerated) on the properties of PMACM could also be studied.

References

Adedeji A., Grunfelder T., Bates F. S., Macosko C. W. Gardiner S. M., and Newcomb D.E. (1996), "Asphalt Modified by SBS Triblock Copolymer: Structures and Properties", *Polymer Engineering and Science,* 36(12): 1707-1723.

Airey G. D., Rahimzadeh B., and Collop A. C., (2004), "Linear Rhelogical Behavior of Bituminous Paving Materials", *Journal of Materials in Civil Engineering,* 16(3): 212-220.

Ait-Kadi A., Brahimi B., and Bousmina M. (1996), "Polymer Blends for Enhanced Asphalt Binders", *Polymer Engineering and Science*, V.36. No.12, pp: 1724-1733.

Al-Dubabe I.A., Al-Abdul Wahhab H.I., Asi I.M., and Ali M.F. (1998), "Polymer Modification of Arab Asphalt", *ASCE Material Journal*, 10(3): 161-167.

Ali M., Al-Abdul Wahhab H.I., Asi I. and Al-Dubabe I. (1999), "Characterization of Polymer Modified Gulf Asphalts", *Petroleum Science and Technology*, 17(12): 125-146.

Amirkhanian S. N., and Williams B., (1993), "Recyclablity of Moisture Damaged Flexible Pavements", *Journal of Materials in Civil Engineering,* 5(4): 510-530.

Anderson R. M., Walker D. E., Turner P. A., (1999), "Low-Temperature Evaluation of Kentucky Performance-Graded 70-22 Asphalt Binders", *Transportation Research Record*, 1661 (Hot-Mix Asphalt Binders): 69-74.

Anderton G.L. (1991). "Modified Asphalt Binders for Military Airfield Pavements", *Proc. AAPT*, 60.

Bahia H.U., Hanson D. I., Zeng M., Zhai H., Khatri M.A., and Anderson R. M., (2001), "Characterization of Modified Asphalt Binders in Superpave Mix Design", *NCHP Report 459*, National Academy Press, Washington D.C.

Bahia H.U. and Davies R., (1994), "Effect of Crumb Rubber Modifiers on Performance Related Properties of Asphalt Binders", *Proc. AAPT*, 63, pp: 414-450.

Baig M. G., and Wahhab, H. I. A., (1998), "Mechanistic Evaluation of Hedmanite and Lime Modified Asphalt Concrete Mixtures", *Journal of Materials in Civil Engineering,* 10(3): 153-160.

Barcena R., Martin A. M., Hazlett D., (2002), "Performance-Graded Binder Specification for Surface Treatments", *Transportation Research Record,* 1810 (Bituminous Binders 2002): 63-79.

Berthelot C. F., Allen D. H. and Searcy C. R., (2003), "Method for Performing Accelerated Characterization of Viscoelastic Constitutive Behavior of Asphalt Concrete", *Journal od Materials in Civil Engineering,* 15(5): 496-505.

Blanko R., Rodriguez R., Garcia-Garduno M., Castano V.M., (1996), "Rheological Properties of Styrene-Butadiene Copolymer-reinforced Asphalt", *Journal of Applied Polymer Science*, 61: 1496-1501.

Bonemazzi F., Braga V., Corrieri R., Giavarini C, and Sartori F., (1996). "Characteristics of Polymers and Polymer-Modified Binders", *TRB*, 1535: 36-47.

Bouldin M.G., Collins J.H., and Berker A., (1991), "Rheology and Microstructure of Polymer/Asphalt Blends", *Journal of Rubber Chemistry and Tech*., 67(4): 577-600.

Brule B., Brion Y., and Tanguy A., (1988), "Paving Asphalt Polymer Blends: Relationships between Composition, Structure and Properties", *Proc., AAPT*, 57: 41-64.

Brule B., (1996), "Polymer Modified Asphalt Cements Used in the Road Construction Industry: Basic Principles", *TRB*, 1535: 48-53.

Carreau P. J., Bousmina M., and Bonniot F., (2000), "The viscoelastic properties of Polymer-Modified Asphalt", *The Canadian Journal of Chemical Engineering*, 78(3): 495-502.

Challa A., Ciochina O. G., Roy C., and Bousmina M., (1997), "Rheological Properties of Bitumen Modified with Used Tyre-Derived Pyrolytic Oil Residue", *Polymer Recycling*, 3(1): 1-14.

Challa A., Roy C., and Ait-kadi A., (1996), "Rheological Properties of Bitumen Modified with Pyrolytic Carbon Black", *Fuel*, 75(13): 1575-1583.

Chebil S., Challa A., Roy C., (1996), "Modification of Bitumen with Scrape Tyre Pyrolytic Carbon Black. Comparison with Commercial Carbon Black Part I: Mechanical and Rheological Properites", *Polymer Recycling*, 2(4): 257-269.

Chen J., Lin K., Young S., (2004), "Effects of Crack Width and Permeability on Moisture-Induced Damage of Pavements", *Journal of Materials in Civil Engineering,* 16(3): 276-282.

Collins J.H., and Bouldin M.G., (1991), "Stability of Straight and Polymer Modified Asphalts", *TRB*. 1342: 92-100.

Denning J.H., and Carswell J., (1981), "Improvements in Rolled Asphalt Surfacing by the Addition of Organic Polymers", *TRRL Report 989.*

El-Mubarak A. H., Sheikheldin S. Y., Fayad N. M., Khaja N., (1999), "Development of a Simple Monitoring Technique for Oil pollution in Sediment", *J Environ Sci Health,* A34(2):391-404.

Fawcett A.H., McNally T., (2001), "Studies on Blends of Acetate and Acrylic Functional Polymers with Bitumen", *Macromolecular Material of Engineering*, 286(2): 126-137.

Fawcett A.H., McNally T. M., (2000a), "Blends of bitumen with various polyolefins", *Polymer,* 41: 5315-5326.

Fawcett A.H., McNally T.M., (2000b), "A Dynamic Mechanical and Thermal Study of Various Rubber-Bitumen Blends", *Journal of Applied Polymer Science*, 76: 586-601.

Gao Gt., Zhang Y., Zhang YX., Sun K, Fan YZ, (2002) "Improved Storage Stability of LDPE/SBS Blends Modified Asphalt", *Polymers & Polymer Composites,* 10(3), pp: 229-236.

García-Morales M, Partal P, Navarro F J, Martinez-Boza F, Mackley M R, Gallegos C (2004) "The rheology of recycled EVA/LDPE modified bitumen", *Rheologica Acta,* in press.

Goodrich J. L., (1991), "Asphaltic Binder Rheology, Asphalt Concrete Rheology and Asphalt Concrete Mix Properties", Drat Prepared for the Association of Asphalt Paving Technologists Seattle 1991 Paper Committee: 1-46.

Goodrich J. L., (1988), "Asphalt and Polymer Modified Asphalt Properties Related to the Performance of Asphalt Concrete Mixes", *Asphalt Paving Technology,* 57: 116-175.

Hameed T, Hussein I. A., (2002), "Rheological Study of the influence of Mw and Comonomer Type on the miscibility of m-LLDPE and LDPE", *Polymer*, 43: 6911-6929.

Hansen K. R., Anderton G., (1993), "A Laboratory Evaluation of Recycled Tire Rubber in Hot-Mix Asphalt Paving Systems", *ASTM Special Technical Publicaiton,* STP 1193: 69-83.

Ho S. M. S., Zanzotto L., and MacLeod D., (2002) "Impact of Different Types of Modification on Low-Temperature Tensile Strength and $T_{critical}$ of Asphalt Binders", *Transportation Research Record 1810*, Paper No. 02-2578: 1-8.

Huffman J.E., (1980), "The Use of Ground Vulcanized Rubber in Asphalt. Asphalt Pav. Construction", *New Materials and Technique, ASTM STP 724.*

Hussein I. A., Iqbal M. H., Al-Abdul Wahhab H. I., (2004), "Influence of M_w of LDPE and Vinylacetate Content of EVA on the Rheology of Polymer Modified Asphalt", *Rheologica Acta*, in press.

Hussein I. A., Ho K, Goyal S. K., Karbashewski E, Williams MC (2000), "Thermomechanical Degradation in the Preparation of Polyethylene Blends", *Polymer Degradation & Stability,* 68(3):381-392.

Hınıslıoğlu S., and Ağar E., (2004), "Use of Waste High Density Polyethylene as Bitumen Modifier in Asphalt Concrete Mix", *Materials Letter,* 58: 267-271.

Isacsson U., and Lu X., (1999), "Laboratory Investigation of Polymer Modified Bitumens", *Journal of the Association of Asphalt Paving Technology (AAPT),* 68: 35-63.

Isacsson U., and Zeng H., (1997), "Relationship Between Bitumen Chemistry and Low Temperature Behavior of Asphalt", *Construction and Building Materials*, 11(2): 83-91.

Isacsson U., and Lu X., (1995), "Testing and Appraisal of Polymer Modified Road Bitumens- State of the Art", *Materials and Structures*, 28: 139-159.

Isacsson U., and Zeng H., (1998), "Low-Temperature Cracking of Polymer-Modified Asphalt" *Journal of Materials and Structures*, 31: 58-63.

Isacsson U., and Zeng H., (1998), "Cracking of Asphalt at Low Temperature as Related to Bitumen Rheology", *Journal of Materials and Structures*, 33(8): 2165-2170.

Isam A. M., (2003), "Performance Modification of Saudi-Asphalt Binders Using SABIC Polymers" MS Thesis (KFUPM).

Jew P., Shimizu J. A., Svazic M., and Woodhams R. T., (1986), "Polyethylene-Modified Bitumen for Paving Applications" *Journal of Applied Polymer Scinence,* 31: 2685-2704.

Jian-Shiuh C. P.E., Liao M., and Shiah M., (2002), "Asphalt Modified by Styrene-Butadiene-Styrene Triblock Copolymer; Morphology and Model", *Journal of Materials in Civil Engineering*, 14(3): 224-227.

Jin H., Gao G., Zhang Y, Zhang Y., Sun K., and Fan Y., (2002), "Improved Properties of Polystyrene-Modified Asphalt Through Dynamic Vulcanization", *Polymer Testing*, 21: 633-640.

Johansson L. S., and Isacsson U., (1998), "Effect of filler on Low Temperature Physical Hardening of Bitumen", *Construction and Building Materials*, 12: 463-470.

Knorr D. B., Jr., Davison R. R., & Glover C. J., "Effect of Various Ageing Techniques on Asphalt Low-Temperature Properties", *Transportation Research Record 1810,* Paper No. 02-3223: 9-16.

Krishnan J. M., and Rao C. L., (2001), "Permeability and Bleeding of Asphalt Mixture using Theory" *International Journal of Engineering Science,* 39: 611-627.

Lee Y., France, L.M., and Hawley M.C., (1997), "The Effect of Network Formation on the Rheological Properties of SBR Modified Asphalt Binders", *Rubber Chemistry and Technology*, 70: 256-263.

Lu X., and Isacsson U., (2002), "Effect of Ageing on Bitumen Chemistry and Rheology", *Construction and Building Materials,* 16: 15-22.

Lu X., and Isacsson U., (2001a), "Modification of Road Bitumens with Thermoplastic Polymers", *Polymer Testing*, 20: 77-86.

Lu X., and Isacsson U., (2001b), "Effect of Binder Rheology on the Low-Temperature Cracking of Asphalt Mixtures", *Road Materials and Pavement Design,* 2(1): 29-47.

Lu X., and Isacsson U., (2000a), "Artificial Ageing of Polymer Modified Asphalt", *Journal of Applied Polymer Science*, 76: 1811-1824.

Lu X., and Isacsson U., (2000b), "Laboratory Study on the Low Temperature Physical Hardening of Conventional and Polymer Modified Asphalt", *Construction and Building Materials*, 14: 79-88.

Lu X., and Isacsson U., (1998), "Effect of Filler on Low Temperature Physical Hardening of Bitumen", *Construction and Building Materials,* 12: 463-470.

Lu X., and Isacsson U., (1997), "Chemical and Rheological Evaluation of SBS Polymer Modified Bitumens", *Fuel*, 77(9/10): 961-971.

Lu X., and Isacsson U., (1997a), "Characterization of SBS Polymer Modified Bitumens-Comparison of Conventional Methods and Dynamic Mechanical Analysis", *ASTM Journal of Testing and Evaluation*, 25: 383-390.

Lu X., and Isacsson U., (1997b), "Compatibility and Storage Stability of Styrene-Butadiene-Styrene Copolymer Modified Bitumens", *Materials and Structures*, 30: 618-626.

Lu X., and Isacsson U., (1997c), "Rheological Characterization of SBS Copolymer Modified Bitumens", *Construction and Building Materials*, 11(1): 23-32.

Lu X., and Isacsson U., (1997d), "Influence of Styrene-Butadiene-Styrene Polymer Modification on Bitumen Viscosity", *Fuel*, 76(14/15): 1079-1180.

Lu X., Isacsson U., and Ekblad J. (1999a), "Phase Separation of SBS Polymer Modified Bitumens", *Journal of Materials of Civil Engineering*, 11: 51-57.

Lu X., Isacsson U., and Ekblad J., (1999b), "Rheological Properties of SEBS, EVA and EBA Polymer Modified Bitumens", *Materials and Structures*, 32: 131-139.

Lu X., Isacsson U., and Ekblad J., (1998), "Low Temperature Properties of Styrene-Butadiene-Styrene Polymer Modified Bitumens", *Construction and Building Materials*, 12: 405-414.

Metcalf J. B., Gopalakrishnan K., and Waters M. D., (2000), "An Initial Investigation of the Rubber Waste (EPDM) in Asphalt Concrete Mixtures", *Waste Management Series,* Waste Materials in Construction: 940-952.

Muncy H. W., King G. N., and Prudhomme B., (1987), "Improved Rheological Properties of Polymer-Modified Asphalts", ASTM Special Technical Publication, 941 (Asphalt Rheology): 147-165.

Murphy M., O'Mahony M., Lycett C., and Jamieson I., 2001, "Recycled Polymers for Use as Bitumen Modifiers", *Journal of Materials in Civil Engineering*, 13(4): 306-314.

Nair N. R., Mathew N.M., Thomas S., Chatterjee P., and Siddiqui M.A., (1998), "Physical and Rheological Characteristics of Liquid Natural Rubber Modified Bitumen" *Journal of Applied Polymer Science*, 68: 53-61.

Panda M., and Mazumder M., (2002), "Utilization of Reclaimed Polyethylene in Bituminous Paving Mixes", *Journal of Materials in Civil Engineering,* 14(6): 527-530.

Parkar F., Brown E. R., (1992), "Effects of Aggregate Properties on Flexible Pavement Rutting in Alabama", *ASTM Special Technical Publication*, STP 1147: 68-89.

Perdomo C., Button J. W., and Lytton R. L., (1992), "A New Approach for Prediction of Permanent Deformation", *ASTM Special Technical Publication,* STP 1147: 295-309.

Petersen K. (1993), "Specifier's Guide to Asphalt Modifiers", *Roads and Bridges Magazine*, May.

Polacco G., Vacin O. J., Biondi D., Stastna J. and Zanzotto L., (2003), "Dynamic Master Curve of Polymer Modified Asphalt from Three Different Geometries", *Applied Rheology,* 13(3): 118-124.

Rakesh K. G., (2000) "Polymer And Composite Rheology, 2nd Edition", Marcel Dekker Inc. New York: 34-62.

Rassamdana H., Dabir B. and Nematy M., Farhani M., and Sahimi M., (1996), "Asphalt Flocculation and Deposition: I. The Onset of Precipitaiton", *AIChE Journal,* 42(1): 10-22.

Romero P., Youtcheff J. and Stuart K., (1999), "Low-Temperature Physical Hardening of Hot-Mix Asphalt", *Transportation Research Record*, 1661 (Hot-Mix Asphalt Binders): 22-26.

Rozeveld S.,J., Shin E.E., Bhurke A., France L., and Drzal L.T., (1997), "Network Morphology of Polymer Modified Asphalt Cements" *Microscopy Research and Technique*, 38: 529-543.

Sabbagh A. B., and Lesser A. J., (1998), "Effect of Particle Morphology on the Emulsion Stability and Mechanical Performance of Polyolefin Modified Asphalts", *Polymer Engineering and Science,* 38(5): 707-715.

Simenson E., Janoo V. C., Member, ASCE, and Isacsson U., (1997) "Prediction of Pavement Response During Freezing and Thawing Using Finite Element Approach", *Journal of Cold Regions Engineering,* 11(4): 308-323.

Singh B., Tarannum H., and Gupta M., (2003), "Use of Isocyanate Production Waste in the Preparation of Improved Waterproofing Bitumen" *Journal of Applied Polymer Science*, 90: 1365-1377.

Singh B., Gupta M, Tarannum H, (2003), "Mastic of Polymer-Modified Bitumen and Poly(vinyl chloride) Wastes" *Journal of Applied Polymer Science*, 90: 1347-1356.

Srivastava A., Hopman P. C., and Molenaar A. A. A., (1992), "SBS Polymer Modified Asphalt Binder and its Implication on Overlay Design", *ASTM Special Technical Publication,* STP 1147: 309-329.

Stastna J., Zanzotto L., and Vacin O. J., (2003), "Viscosity Function in Polymer Modified Asphalt", *Journal of Colloid and Interface Science*, 259(1): 200-207.

Stastna J., Zanzotto L., and Vacin O., (2000) "The Changes in Thermomechanical Properties of the Base Asphalt by Some Polymer Modifiers", XIIIth International Congress on Rheology, Cambridge: 4-4 to 4-6.

Stastna J., and Zanzotto L., (1999), "Linear Response of Regular Asphalt to External Harmonic Fields", *Journal of Rheology*, 43(6): 719-734.

Stastna J., and Zanzotto L., (1999), "Response to Comment on the Thermorheological Complexity and Relaxation Modes of Asphalt Cement", Bituminous Materials Chair Faculty of Engineering University of Calgary, Calgary AB, *Journal of Rheology* (New York) 43(6): 1705-1707.

Terrel R.L., and Epps J.A., (1989), "Using Additives and Modifiers in Hot Mix Asphalt", QI Series 114, NAPA.

Varma R., Takeichi H., Hall J. E, Ozawa Y. F., and Kyu T., (2002), "Miscibility Studies on Blends of Kraton Block Copolymer and Asphalt", *Polymer*, 43: 1-5.

Wang J. X., and Buckley J. S., (2001), "A Two-Component Model of the Onset of Asphaltene Flocculation in Crude Oils", *Energy & Fuels,* 15: 1004-1012.

Wen G., Zhang Y., Zhang YX., Sun K, Fan YZ, (2002), "Rheological Characterization of Storage-Stable SBS-modified Asphalts", *Polymer Testing,* 21: 295-302

Wen G., Zhang Y., Zhang YX., (2002) "Improved Properties of SBS-Modified Asphalt with Dynamic Vulcanization", *Polymer Engineering & Science,* 42(5): 1070-1081.

Widyatmoko I., Ellis C., and Read J. M., (1999), "The Application of Dissipated Energy Method for Assessing the Performance of Polymer-Modified-Bituminous Mixtures", *Materials and Structures,* 32: 304-310.

Wloczysiak P., Vidal A., Papirer E., (1997), "Relationships between Rheological properties, Morphological Characteristics, and Composition of Bitumen-Styrerne Butadiene Styrene Copolymers Mixes. II A thermodynamical Interpretation", *Journal of Applied Polymer Science*, 65: 1595-1607.

Wu C., Liao H., Lai S., (2002), "Study on the Graft Reaction of Maleic Anhydride on to Metallocenen-Based Polyethylene-Octane Elastomer", *Polymer and Plastic Technology & Engineering,* 41(4): 645-661.

Yousefi A.A., (2003), "Polyethylene Dispersions in Bitumen; The effect of the Polymer Structural Parameters" *Journal of Applied Polymer Science*, 90: 3183-3190.

Yousefi A. A., Ait-Kadi A., and Roy C., (2000), "Composite Asphalt Binders: Effect of Modified RPE on Asphalt", *Journal of Materials in Civil Engineering*, 12(2): 113-123.

Zanzotto L., Stastna J, Ho K., (2003), "Characterisation of Regular and Modified Bitumens via Their Complex Modulus" *Journal of Applied Polymer Science* 59: 1897-1905.

Zanzotto L., Stastna J., Bouldin M. and Jhanwar D., (2000), "Performance Specifications- What is Too Little, What is Too Much", in *Proc. Of 1st International Conference World of Asphalt Pavements,* Sydney, Australia: 958-972.

Zanzotto L., Stastna J., and Ho S., (1999), "Molecular Weight Distribution of Regular Asphalts from Dynamic Material Functions", *Material and Structures*, 32(217): 224-229.

Zanzotto L., Stastna J., Vacin O., and Bouldin M., (1999), "Performance Related Specification and Asphalt Binders Prepared by Different Technologies", *Petroleum and Coal,* 41(3-4): 127-137.

Zanzotto L., Stastna J., and Ho K., (1996), "Characterization of Regular and Modified Bitumens via Their Complex Modulus", *Journal of Applied Polymer Science,* 59: 1897-1905.

Zhou H., Nodes S. E., and Nichols J. E., "Evaluation of Three Polymer Modified Asphalt Concretes", *Materials and Construction*, Transportation Research record, No.1454: 181-192.

Zoorob S. E., and Suparma L. B., (2000), "Laboratory Design and Investigation of the Properties of Continuously Graded Asphaltic Concrete Containign Recycled Plastics Aggregate Replacement (Plastiphalt)", *Cement & Concrete Composites,* 22: 233-242.

Zupancic A., and Zumer M., (2002), "Rheological Examination of Temperature Dependence of Conventional and Polymer-Modified Road Bitumens", *The Canadian Journal of Chemical Engineering*, 82(2): 253-263.

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